Los Alamos National Laboratory

Actinide Research Quarterly

Highlights of the
PLUTONIUM FUTURES—
THE SCIENCE CONFERENCE 2003

1943 - 2003

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Ideas That Change the World

Actinide Research Quarterly

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Plutonium Futures—
The Science Conference 2003

More than 1,000 tons of plutonium exist throughout the world in the form of used nuclear fuel, nuclear weapons components, various nuclear inventories, legacy materials and wastes. It is clear that large inventories of plutonium must be prudently managed for many decades. A complex blend of global political, socioeconomic and technological challenges must be overcome to manage these inventories efficiently and safely.

From a technological perspective, plutonium is one of the most complex elements in the Periodic Table. The metal exhibits six solid allotropes at ambient pressure and its phases are notoriously unstable with temperature, pressure, chemical additions and time. Plutonium sits near the middle of the actinide series, which marks the emergence of 5f electrons in the valence shell. Elements to the left of plutonium have delocalized (bonding) electrons, while elements to the right of plutonium exhibit more localized (non-bonding) character. Plutonium is poised in the middle, and for the delta-phase metal, the electrons seem to be in a unique state of being neither fully bonding or localized, which leads to novel electronic interactions and unusual physical and chemical behavior. The concept of localized or delocalized 5f electrons also pervades the bonding descriptions of many of the plutonium molecules and compounds. An understanding of the electronic structure of the pure element and its compounds continues to challenge both theorists and experimentalists in all areas of plutonium science.

The "Plutonium Futures—The Science Conference" was established to increase awareness of the importance of plutonium research and facilitate communication among its international practitioners.

Conference participants received a specially designed coin (shown at far right) encased with a sample of Trinitite, a greenish, glasslike substance found only at ground zero at Trinity Site in southern New Mexico. The man-made mineral and was formed on July 16, 1945, when the desert sand was melted by the intense heat of the world's first nuclear explosion and then solidified. The coin was designed by Los Alamos' Jay Tracy.

Plutonium Futures— The Science 2003

Moreover, we hope that this series of conferences will stimulate the next generation of scientists and students to study the fundamental properties of plutonium. The 2003 conference, held in July in Albuquerque, N.M., was the third in this series and attracted more than 328 participants from 63 institutions and 12 countries. We were also encouraged by the participation of 42 students, an increase over past years. More than 180 contributed presentations covered the latest results in plutonium condensed matter physics, materials science, compounds and complexes, environmental behavior, detection and analysis, separations and purification, nuclear fuel cycles, and waste isolation and disposal.

In this issue of *Actinide Research Quarterly,* we present some highlights of the 2003 conference in the form of short articles from conference participants, interviews with poster presenters, and reports from ARQ staff.

By increasing the international dialogue through conferences and publications, we hope to facilitate the developing renaissance in plutonium science that will enable efficient solutions to Cold War legacy problems and provide maximum benefits for society from the enormous energy potential of plutonium.

—Gordon D. Jarvinen
David L. Clark

Structural Trends and Bonding of the 5f-Elements (U–Am) with the Oxoligand IO_3^-

A. C. Bean,[1] B. L. Scott,[1] T. Albrecht-Schmitt,[2] and W. Runde[1]

[1]Los Alamos National Laboratory and [2]Auburn University

To assess the environmental impact of transuranium elements (neptunium, plutonium, and americium) on nuclear waste repositories, scientists must better understand the solid-state chemistry of transuranium compounds. Researchers are particularly interested in how these elements might react with fission-product radionuclides, such as iodine-129 in its oxidized and reduced forms, such as the iodide (I^-) or iodate (IO_3^-) ions. Iodate is of particular interest for nuclear waste.

"We used a process known as hydrothermal synthesis (mineral synthesis in the presence of heated water) to produce single crystals, which we used to obtain crystal structures and Raman spectra of five novel transuranium iodates," said Amanda Bean of Los Alamos. "Our end goal was to look at the fundamental chemistry of these iodates for the first time."

The five transuranium iodates are as follows: $NpO_2(IO_3)_2(H_2O)$, $NpO_2(IO_3)_2 \cdot H_2O$, $PuO_2(IO_3)_2 \cdot (H_2O)$, and two forms of $Am(IO_3)_3$. This research presents a vital first step in applying a synthetic approach to unraveling the structural properties of materials that contain the series of the light actinide elements. With such structural properties in hand, researchers will be better able to address issues related to long-term storage and disposition of nuclear materials.

—*Octavio Ramos, Jr.*
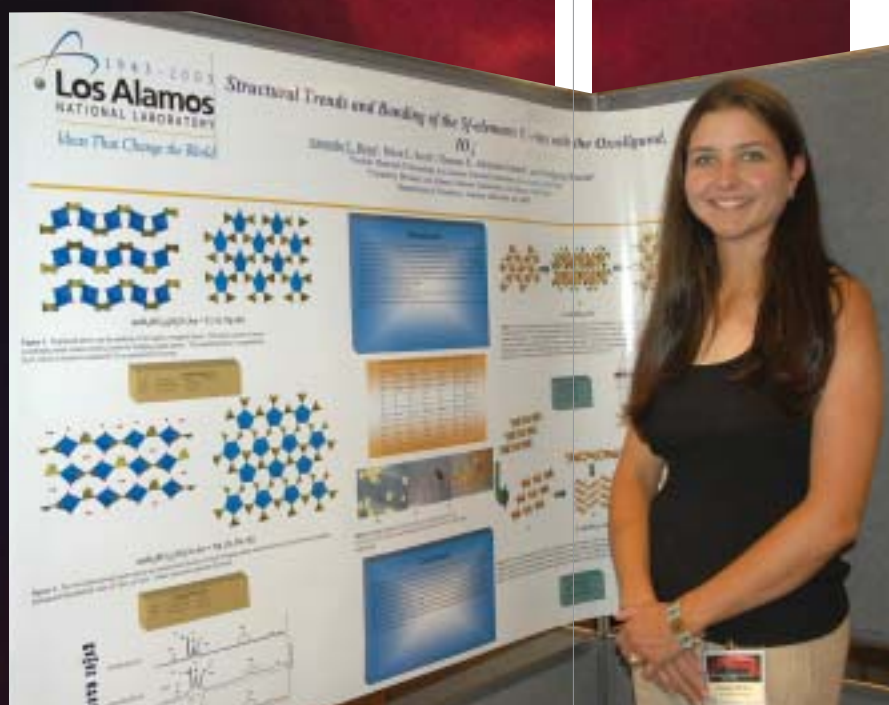
Amanda Bean

Keynote speaker Sig Hecker

Plutonium: Whether boon or risk, both viewpoints must be respected

"Plutonium evokes the entire gamut of human emotions, from good to evil, from hope to despair, from the salvation of humanity to its utter destruction." With typical dramatic flair, Los Alamos Senior Fellow Sig Hecker cut the ribbon on the opening morning of the conference.

Adding the obvious, that "there's no other element in the periodic table that shares such a burden," Hecker then surged into a historical perspective. Its backdrop was the dual-use scenario of domestic power and nuclear weapons—drawing energy from an atomic nucleus that can be tapped for "a factor of increase in millions of energy production."

Beginning with President Eisenhower's 1953 Atoms for Peace initiative, Hecker outlined the period of intense international collaboration on the peaceful uses of atomic energy that spanned the period from the 1955 First International Congress in Geneva through the end of the Cold War. In Hecker's view, the late 1980s marked a period of diminished collaboration, while the first Plutonium Futures Conference in 1997 symbolized the "attempt to regenerate" the spirit of international collaboration in plutonium science.

Hecker's post-1997 review adopted a sociopolitical angle, citing the cooperative endeavors whereby the United States and Russia continue to reduce their arsenals of nuclear weapons. He reviewed such initiatives as burning excess weapons plutonium for peaceful energy production and blending-down Russia's declared 500-ton excess of highly enriched uranium to low-enriched uranium. Some of the latter has already been purchased by the United States for its light-water electricity-generating reactors. In addition, Hecker discussed what he characterized as significant enhancements in the security of nuclear materials and a reduction in the level of nuclear-materials trafficking.

On the flip side, Hecker raised concerns deriving from the "horizontal proliferation" of nuclear weapons in Asia, including radiological-terrorism concerns following the events of 9/11/01, which "indicate that we do not live in a very peaceful world." He also commented on the challenges of dealing with the legacy waste of the nuclear era, citing specific instances in both the United States and Russia and including the decommissioning and dismantlement of the latter's nuclear submarine fleet.

Never one to end on a sour note, Hecker noted the resurgence in nuclear-power research in the United States, mentioning both fuel-cycle initiatives and the positive connotations of "discussions about the construction of nuclear power plants . . . for the first time in a couple of decades."

Referring to opinions that plutonium is either our greatest boon or our greatest risk, Hecker cautioned that "we must respect both points of view." He then rolled into the day's events by declaring that "no matter what you believe about the political challenges, scientifically, plutonium is without question the most complex and fascinating element . . . and that's, after all, why we're here this week."

Finally, in calling for a continued international collaboration to solve scientific and sociopolitical challenges, Hecker concluded by expressing the hope that "this conference will, in particular, stimulate interest in the younger generation in carrying on the challenges and all those things that we have yet to learn associated with plutonium and the other actinides."

—Vin LoPresti

Sig Hecker

Theory of Positron Annihilation in Helium-Filled Bubbles in Plutonium

P. A. Sterne and J. E. Pask

Lawrence Livermore National Laboratory

Scientists at Lawrence Livermore National Laboratory (LLNL) have developed a first-principles, finite-element-based method to calculate positron lifetimes for defects in metals. This method can treat system cell sizes of several thousand atoms, thus enabling researchers to model defects in plutonium that range in size from mono-vacancy to helium-filled bubbles of more than 1 nanometer in diameter.

"Our objective is to perform some theoretical calculations that can help us interpret positron annihilation experimental data," said Phillip Sterne of LLNL. "Recent experiments at Livermore have identified two lifetime components in aged plutonium samples, one at around 182 picoseconds and another at about 350 to 400 picoseconds. But what do these values mean? What's the interpretation? To understand what they mean, we've been doing first-principles calculations using a modeling technique that can help us interpret which defects are responsible for the lifetime components we are observing during our experiments."

Sterne noted that positrons are great probes for defects. Positrons are attracted to the nanosized defects found in the alloy. As the positrons decay, they release energy in the form of gamma rays. Gamma rays produce a distinct signature that helps scientists identify the size, quantity, and type of defect in an alloy.

When helium atoms are introduced into vacancy clusters, the positron lifetime is reduced. The modeling studies indicate that the experimentally observed positron lifetimes in aged plutonium metal are consistent with the presence of two to three helium atoms per vacancy.

—Octavio Ramos, Jr.

Retired
Los Alamos
Scientist
**Robert
Penneman**
(left) and
**Phillip
Sterne**

Tutorial
A plutonium potpourri

Dave Clark

Challenges in plutonium physics and chemistry

Seaborg Institute Director David Clark kicked off an approximately four-hour plutonium tutorial designed to "stimulate the next generation of scientists and students." He framed his discussion in the most interesting way possible, that is, in terms of the metal's chemical and metallurgical peculiarities. From the uniqueness of its oxidation-state behavior (whereby, under certain conditions, plutonium solutions can simultaneously exhibit the presence of three or four different oxidation states) to the different crystal structures and physical properties of its allotropes (physical phases), the discussion accurately reflected the reason why so many scientists worldwide are engaged in the study of a single chemical element and its compounds.

"I'm going to walk you through some of the interesting scientific challenges that will be addressed at the conference," Clark offered, and he quickly delivered on the promise, covering the areas of stockpile, materials, and environmental stewardship. His focus was the phenomenon of nuclear materials aging, and he used an example of an aged tanker that had recently broken apart off the coast of Spain to generally frame the issue's importance.

Clark did not ignore the fact that, as science often does, a seemingly completely negative characteristic has also been harnessed for positive applications. Most notable was the use of plutonium-238 as a heat and power source in space missions, particularly the Mars Rover projects in which Los Alamos plutonium scientists have been intimately involved. Additionally, Clark predicted that because of self-irradiation-based changes occurring in plutonium-based superconductors over time, "plutonium will teach us quite a bit about superconductivity mechanisms."

IAEA activities in plutonium nonproliferation and security

The tutorial's second presentation, given by Graham Andrew of the International Atomic Energy Agency (IAEA), proved to be a pertinent segue, particularly in light of recent international events precipitating concern over nuclear terrorism. He reviewed how the agency functions and interacts with national states and emphasized the ongoing challenge implicit in "checking whether what you measure can possibly be what you're told."

Of particular interest were new analytical tools developed to assay plutonium samples for isotope ratio, as well as to determine the content of minor actinides such as neptunium, americium, and curium. Also of interest was the revelation that, in addition to its central offices in Vienna, the agency maintains laboratories at certain large nuclear-fuel reprocess-

Graham Andrew

ing plants such as the one at Rokkashamura, Japan. This need was highlighted by the statistic that mixed-oxide (MOX) fuel requirements for commercial light-water reactors comprise about 190 metric tons per year, compared with only 24 tons per year currently being produced by reprocessing.

Andrew also discussed the limitations of traditional safeguards and the efforts to expand safeguards by getting nations to "sign on to more wide-ranging access and forensic environmental sampling . . . from mines to nuclear waste" and via expanded inspector training to

help enhance each individual inspector's recognition capabilities. This concern extended to the proliferation resistance of future energy systems, in the sense of "making that nuclear material less attractive to a proliferator." This IAEA initiative is, of course, particularly relevant since the events of 9/11/01, with the subsequent increased concerns about sabotage and radiological terrorism ("dirty bombs").

The nuclear fuel cycle and new initiatives

In comparing the broad outlines of so-called "once-through," "European/Japanese," and "advanced proliferation-resistant" nuclear fuel cycles, Edward Arthur's presentation was eminently pragmatic. Arthur, former Los Alamos acting office director for nuclear technology and applications, cited the requirement for reprocessing of spent fuel as the first step in any of the cycles. He then made it clear that the cost of spent-fuel reprocessing did not currently compare very favorably with the reprocessed fuel's electricity value.

He stressed that "front-end" operations such as decladding, storage, and separations, and back-end waste-management components collectively accounted "for 75 percent of the cost of a fuel reprocessing facility." But he was also unequivocal in his view that economic issues had to be "looked at from an overall system perspective."

Regardless of the obstacles, the U.S. Senate's FY04 budget includes a funding target of $78 million for the multi-laboratory Advanced Fuel Cycle Initiative and authorizes a study of a demonstration hydrogen-producing nuclear power plant. Ultimately however, to achieve the goals of Power for the Twenty-First Century, reprocessing must handle tens of thousands of tons of spent nuclear fuel. It must also deal with such factors as radiation, criticality, and chemical hazards such as strong acids and solvents—what Arthur characterized as "major technical issues still facing reprocessing."

Colloid-facilitated transport of plutonium

The afternoon's final presenter was Annie Kersting of Lawrence Livermore National Laboratory. "What we really want to understand is the life cycle of a colloid," Kersting said, and she proceeded to explain why this was a vital goal to chemists trying to sort out the complexities of plutonium's interaction with the natural environment.

Mobile particulates generally smaller than 1 micron, colloids originate from a diversity of environmental sources; and both organic (carbon-based) and inorganic (mineral-based) colloids are ubiquitous in soil and water. Understanding colloids and their significance in environmental transport of plutonium and other actinides thus entails a combination of geology, hydrology, and chemistry, as Kersting's presentation illuminated at every turn.

As such, she discussed the need for field studies to firmly foot laboratory experiments and theory in the local geology and hydrology of sites such as Rocky Flats and Savannah River. Such local geochemistry determines if colloids will or will not facilitate the transport of plutonium or other actinides through the environment.

Kersting explained that these studies have so far painted an incredibly complex landscape for actinide transport, since both adsorption and desorption had to be assessed and because "measuring the concentration of colloids in water is very difficult." For example, "you may see plutonium sorb very strongly to say silica and iron oxide, and then you go down a few meters, and it may desorb off that silica but still stay on the iron oxide."

Kersting summarized her talk by framing the overall issue as an imperative to understand the fundamental chemistry of actinide nanoparticles.

—*Vin LoPresti*

Edward Arthur

Annie Kersting

Understanding and Predicting Plutonium Alloys Aging: A Coupled Experimental and Theoretical Approach

N. Baclet,[1] P. Pochet,[1] Ph. Faure,[1] C. Valot,[1] L. Gosmain,[1] Ch. Valot,[2] J. L. Flament,[3] and C. Berthier[3]

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Defects in a plutonium alloy begin at the atomic level. Once created, such defects can diffuse, leading to changes in the physical properties of the alloy. Such changes in turn may affect the reliability and safety of a nuclear weapon.

To better understand and thus better predict aging effects of plutonium alloys, scientists in France have embarked on a multiscale approach that involves both theoretical and experimental components. The two-pronged challenge is to identify which aging parameters are relevant for modeling and develop experimental techniques that can measure such physical parameters.

One parameter relevant for modeling is the interatomic potential, which is the key to modeling displacement cascades using molecular dynamics. The interatomic potential is intimately related to the elastic constants of the plutonium-gallium alloys of interest. Scientists in France are developing x-ray diffraction techniques to determine these values.

"We have tested this technique on pure copper and rhodium samples because the mechanical properties of these materials are similar to those of delta-plutonium," said Nathalie Baclet of CEA–Centre de Valduc. "Preliminary results are promising. We are now improving the technique so that it takes into account the material's texture."

—Octavio Ramos, Jr.

Nathalie Baclet

Plutonium-238 metal as a multiphase system

Previous investigations at the Research Institute of Atomic Reactors of plutonium metal containing more than 80 percent plutonium-238 show a number of physical properties in the metal that are considerably different from those found in ordinary "low-radioactivity" plutonium-239. For example, the hydrostatic densities of plutonium-238 samples are always substantially lower than those of similarly treated samples of plutonium-239 (by 1.1–2.3 grams per cubic centimeter [g/cm^3] and more). More details can be found in an article in *Radiochemistry* (English), 2001, Vol. 43, pages 111-117.

When a special thermomechanical treatment is used on plutonium-238 samples, the densities increase only for a short time. The densities decrease quickly after pressure is released and the shapes of the samples become distorted.

Other differences between the two isotopes can be seen in the thermograms of plutonium-238 as the temperature is increased. The intensities of peaks of the alpha to beta, beta to gamma, and gamma to delta ($\alpha\rightarrow\beta$, $\beta\rightarrow\gamma$, $\gamma\rightarrow\delta$) allotropic transformations are always substantially lower than those of the corresponding plutonium-239 material. Plutonium-238 also has a temperature coefficient of electrical resistivity that is lower in the region of the alpha-phase field as well as some other differences in the temperature dependence of electrical resistance.

A combination of the effects observed in plutonium-238 metal can be explained by its continuous and intensive self-irradiation, which results in co-existence of the known plutonium crystal modifications in this metal at room temperature. To understand the nature of these differences, samples of various ages were studied using x-ray diffraction to reveal the crystal structure of the plutonium-238 metal and to discern how specific alpha radioactivity and self-irradiation (aging) affect this structure.

Results

The metal samples each had different plutonium-238 content and were not subjected to compression loads. They were composed of micron-thick layers of plutonium-238 condensed at high temperature and high vacuum onto flat tantalum substrates. Moreover, these samples did not contain radiogenic helium in the initial state.

The table below lists the properties of these samples. Samples 1, 2, and 3 were considered high-radioactivity metals, sample 4 was labeled as medium radioactivity, and sample 5 was low radioactivity.

The samples were prepared, kept, and investigated under similar conditions. All of them had a comparable purity and, according to the spectral analysis results, did not contain certain impurities in the quantities sufficient to stabilize the "temperature" modifications of plutonium. The x-ray

Characteristics of plutonium samples

Sample	Atomic fraction of ^{238}Pu, %	Mass, mg	Thickness, µm	Alpha-radioactivity*
1	86.5	3.5	6–8	240
2	86.5	0.5	0.8–1.0	240
3	86.5	21	37–46	240
4	5.8	10	18–22	17
5	1.1	8	14–18	4

*With reference to ^{239}Pu isotope

Contributed Papers

Changes in the phase compositions of the high-radioactivity (1, 2) and "low-radioactivity" (5) plutonium samples during their aging.

analysis was performed within about a one-year aging timeframe of the samples at room temperature.

Only the alpha-phase diffraction peaks were observed in the "low-radioactivity" plutonium x-ray patterns (sample 5) during the whole period of the investigation (see table below). Individual diffraction peaks of the "high-temperature" modifications (beta, gamma, delta, and, probably, delta-prime) were recorded in the

Sample	τ^*, day	Allotropic plutonium modification**					
		α	β	γ	δ	δ'	ε
1	1	±	+	+	+	+	−
	20	+	±	+	+	−	−
	40	+	±	+	+	+	−
	60	+	+	+	+	+	−
	98	+	±	±	+	−	−
	343	+	±	−	+	−	−
2	1	±	±	±	+	−	−
	43	+	+	+	+	+	+
	52	+	+	+	+	±	±
	101	+	+	+	+	±	−
	339	+	−	−	+	−	−
5	1	+	−	−	−	−	−
	343	+	−	−	−	−	−

* Aging period

*** «−» no diffraction peaks of this lattice;
«±» individual peaks of this lattice;
«+» sufficient peaks to calculate the parameters of this lattice*

x-ray patterns of the "medium" specific alpha-radioactivity plutonium (sample 4) along with the strong alpha-plutonium peaks.

A unique phenomenon of the dynamic co-existence of four, five, and even six allotropic modifications of plutonium was observed in samples 1, 2, and 3 of high-radioactivity metal.

During the long-term aging of high-radioactivity samples 1, 2, and 3 and "mid-radioactivity" sample 4, a slow process of changes in their phase compositions was recorded: a relative decrease in the content of the " high-temperature" low-density modifications and an increase in the content of the high-density alpha-phase of plutonium.

In samples 1, 2, and 3, a ratio of the total intensity of the (020) and (211) alpha-plutonium diffraction peaks to the total intensity of the (111) delta-plutonium, (111) gamma-plutonium, and (101) delta-prime-plutonium peaks was designated as criterion C of this process. A number of transformation stages can be found on the curves resulting from plotting the value of criterion C versus the age of the sample since fabrication. The figure on the next page presents the curve for sample 3 as an example. A similar curve was also obtained for "mid-radioactivity" sample 4.

The peak-by-peak analysis of the x-ray patterns of the high-radioactivity samples shows that the delta phase in them disappears more slowly than the other "high-temperature" plutonium modifications (see table at left). Nevertheless, at a certain stage of aging these modifications can recur, apparently, as intermediate phases in the (delta to alpha) transformation. So, in samples 1 and 2 within 40- to 60-day aging, the maximum number of the allotropic modifications is recorded (five and even six). At the end of long-term aging (about one year), only the alpha and delta phases are observed by x-ray analysis of the high-radioactivity samples, and no obvious signs of the "high-temperature" phases were revealed in the "mid-radioactivity" sample.

Some peculiarities were revealed on the curves showing the atomic volume changes of the delta-plutonium lattice in sample 3 and of the alpha-plutonium lattice in sample 4. A volume increase at the beginning of self-irradiation results in a "hole" (an abrupt decrease and subsequent recovery of this parameter) after some period of aging. The atomic volumes of the indicated lattices reduce slowly in the course of further aging of the samples.

Discussion

In these experiments with thin layers of plutonium-238 metal deposited on a metal substrate, we have considerably increased the radiation-induced self-damage rate of the metal, but we cannot similarly increase the annealing rate of radiation defects. Therefore, these experiments do not cover the accelerated aging of bulk plutonium metal. A quantitative change in the radiation-defects concentration leads to observable qualitative changes in the metal properties, but this does not change the nature of plutonium. An increase in the specific alpha radioactivity allows a deeper insight into the fundamental properties of plutonium.

The analysis of the experimental results shows that the co-existence of the different allotropic modifications in high-radioactivity plutonium at room temperature is caused both by intensive self-irradiation and the complex phase diagram of plutonium metal. Radiation-induced vacancies and clusters of vacancies appear to play a large role in the formation of the "high-temperature" modifications.

The bonding 5f-orbitals in plutonium have a small overlap; therefore, a considerable relaxation of the lattice can take place near the vacancy and an area with an increased atomic volume (fluctuation of atomic volume) appears. The potential energy of the bonding 5f electrons belonging to the atoms located near the vacancy decreases, the electrons localize (they transfer to the fluctuation states), and "fluctuons" (bound states of electrons and fluctuation) appear.

The bonds typical of one of the "high-temperature" modifications arise inevitably between these atoms with localized 5f electrons. Thus, vacancies in plutonium apparently are nonlocal; they represent an ensemble of atoms with a different bonding pattern forming in the lattice as an entity.

Criterion C versus aging period and calculated content of radiogenic helium in sample 3.
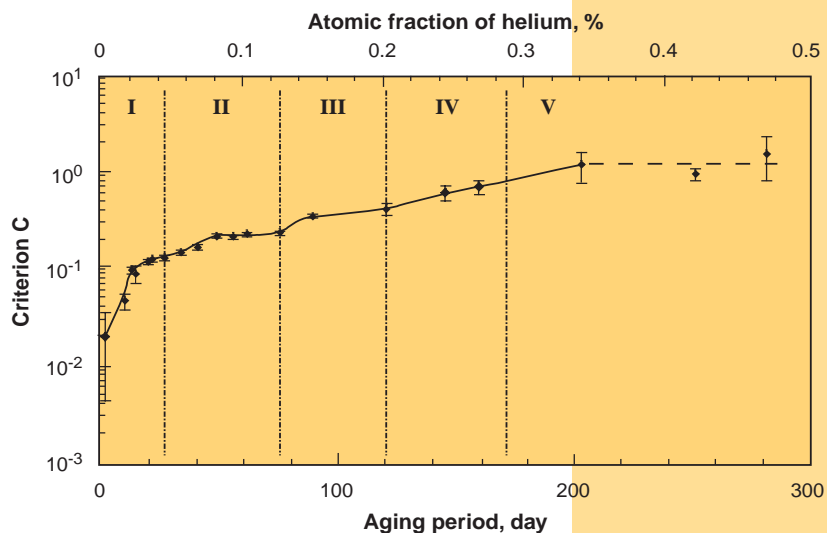
The behavior of "fluctuons" was investigated theoretically by Russian theorist M.A. Krivoglaz. A comparison of properties of the fluctuons with those of plutonium-238 metal allows the so-called "unusual" behavior of this system to be explained.

An increase in the vacancy concentration due to intensive plutonium self-damage leads to an appearance of the "high-temperature" modifications already at room temperature. The crystal lattice around the large vacancy clusters arising in the deceleration regions of recoils is under tension. It provides relative stability of the "high-temperature" phases.

To explain the slow change in the phase composition of high- and "mid-radioactivity" plutonium during long-term aging as well as the complex multistage nature of this process, researchers proposed another mechanism. This was related to accumulation of radiogenic helium and evolution of its forms in the metal, especially in the intragrain cavities. Helium behavior also contributes to the changes in the atomic volumes of plutonium lattices under self-irradiation.

Contributed Papers

Thomas Fanghänel

Thomas Fanghänel of the Institut für Nukleare Entsorgung, Karlsrühe Research Center, Germany, makes a point during his discussion of nanoscopic approaches to aquatic plutonium chemistry.

This article was contributed by Clemens Walther, Claudia Bitea, Jong Il Yun, Jae Il Kim, Thomas Fanghänel, Christian M. Marquardt, Volker Neck, and Alice Seibert of the Institut für Nukleare Entsorgung, Karlsrühe Research Center.

Predicting long-term actinide mobility
Nanoscopic approaches to aquatic plutonium chemistry

The Institut für Nukleare Entsorgung (INE) in Karlsrühe Research Center, Germany, focuses on the basic research relevant to the assessment of prospective repositories for radioactive waste, including both technical and scientific chemical aspects. The predictive modeling of long-term actinide mobility in the geosphere is contingent on basic knowledge of the aquatic chemistry of actinides. In this context, plutonium is of special interest.

Plutonium appears in spent fuel in small amounts (about 1 percent), but after the decay of short-lived fission products, plutonium-239 represents the dominant radioactive inventory for thousands of years.

On the one hand, the solubility constraints of plutonium have led to the perception that this element will be immobilized easily in the repository environment. On the other hand, this particular property of low solubility induces the formation of colloids (tiny, nano-sized particles—either real colloids or pseudo colloids), which may strongly enhance plutonium's potential for mobility in the aquifer. These characteristic properties are of cardinal importance for our work.

Challenges

Different oxidation states (typically III–VI) of plutonium can coexist in aqueous solution under the appropriate conditions, with the relative abundance of each oxidation state depending on the chemical conditions such as pH, Eh, and ionic strength. Plutonium exhibits a complicated redox behavior that permits transformation of one oxidation state into another. For example, the collision of two plutonium(IV) ions generates one plutonium(III) and one plutonium(V) ion, and the plutonium(V) ion subsequently can be oxidized to a plutonium(VI) ion by an additional collision with a plutonium(IV) ion.

Since different oxidation states exhibit different chemical properties, a reliable speciation (with regard to the oxidation states) is required. Our work focuses on the tetravalent plutonium ion, which, in aquatic solution, is known to be unstable even at low pH in dilute concentrations, not only because of disproportionation—the interconversion of its ionic species—but also because of colloid formation.

This instability of dilute plutonium(IV) has made the appraisal of its thermodynamic solubility in aquatic systems extremely difficult, resulting in a large number of controversial results. Thus, assessing the chemical reactions of plutonium(IV) in dilute concentrations in the low pH region requires sensitive speciation and colloid characterization methods.

Our present work combines two different laser spectroscopic speciation approaches, providing the possibility of assessing the chemical reactions of plutonium(IV) at concentrations of only a few micromoles per liter or even lower.

Researchers from the Karlsruhe Research Center Institut für Nukleare Entsorgung are using a "homebuilt" laser setup to study the colloidal transport of plutonium in aqueous solutions. In the front row, from left to right, are: Claudia Bitea and Alice Seibert. In the back row, from left to right, are: Christian Marquardt, Clemens Walther, and Jong Il Yun.

Experimental approaches

We use two methods in our research: laser-induced breakdown detection (LIBD) for colloid quantification and laser-induced photoacoustic spectroscopy (LPAS) for chemical speciation.

LIBD is based on nonlinear interaction of colloids with a tightly focused laser beam (see sidebar on page 14). This leads to the formation of a hot, dense plasma, detected either optically (via light emission) or acoustically (via its expansion-generation shockwave). Each plasma event corresponds to a single colloid and, when compared with the number of laser shots, this provides a measure of colloid concentration.

Compared with dynamic light scattering (the most frequently applied colloid detection technique), the sensitivity, particularly for colloids smaller than 50 nanometers, is enhanced by more than six orders of magnitude. Compared with the so-called single-particle counter, a static light-scattering device, the accessible size range is considerably extended toward smaller colloids.

For particles of 20-nanometer diameter, for instance, the sensitivity corresponds to detecting a pinhead one millimeter in diameter in a good-sized hotel swimming pool.

The speciation methods are based on linear light absorption. Plutonium's oxidation states III, IV, V, and VI exhibit characteristic absorption bands. The absorption strength is directly proportional to the amount of species present. From the (visible) absorption spectra, a quantitative speciation is obtained, typically by UV-visible (UV-Vis) spectroscopy, which measures the extinction (i.e., absorption plus scattering losses) of white light wavelength resolved after passing through the sample.

However, this method is limited to measuring plutonium(IV) concentrations of approximately 10 micromolar. LPAS lowers this limit by a factor of up to 100 by detecting the effects of the light absorbed by the plutonium ions
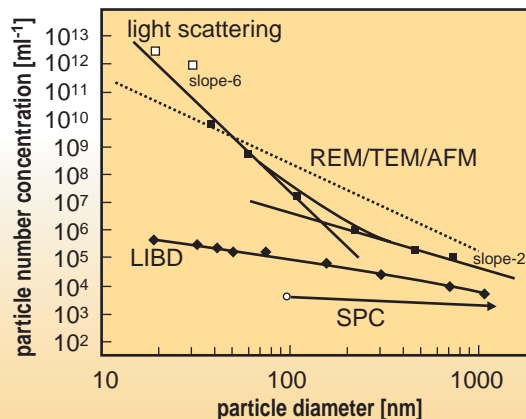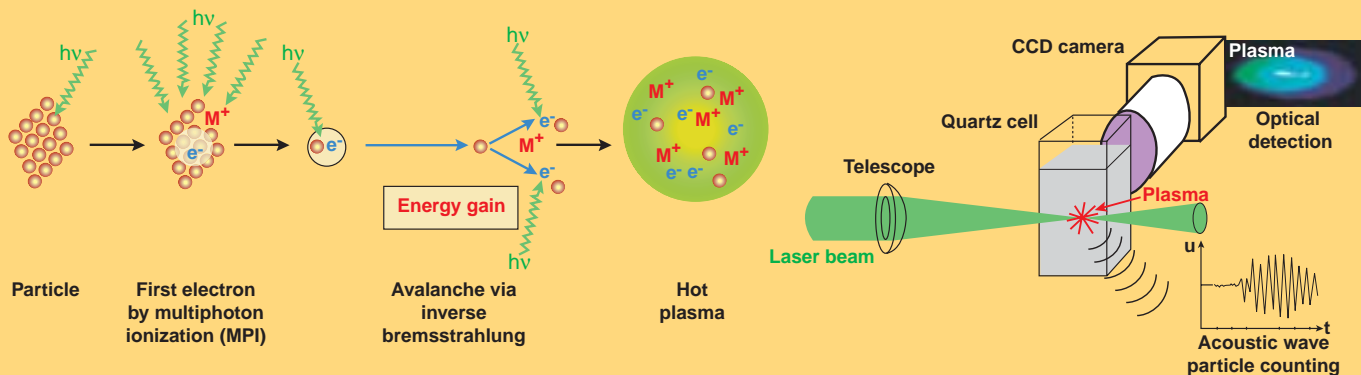

This figure shows the sensitivity of laser-induced breakdown detection (LIBD) compared with classical characterization methods. LIBD's sensitivity is enhanced by more than six orders of magnitude compared with dynamic light scattering, and the accessible size range is considerably extended toward smaller colloids when compared with the single-particle counter (SPC).

(photothermal method) rather than the transmitted light. A 10-nanosecond light pulse of a tunable dye-laser is guided through the sample, and the energy of the absorbed photons gives rise to a rapid temperature increase with subsequent expansion and generation of an acoustic shock wave.

Analogous to the LIBD method, this acoustic wave is detected by a piezo detector, but because its energy content is rather low (less than one nanojoule), the signal is electronically amplified prior to data recording. The acoustic (and electronic) signal is linearly proportional to the absorption strength at the specific wavelength of the laser beam. Absorption spectra are obtained by scanning the laser over the desired spectral range. In addition to the increased sensitivity down to the micromole-per-liter range, LPAS (in contrast to UV-Vis) is not influenced by the presence of colloids, which give rise to light scattering in the blue end of the spectrum.

A time evolution of laser-induced plasma plumes incited on single colloids as observed by an ultrafast (200 picoseconds) charge-coupled device camera.

Particle — **First electron by multiphoton ionization (MPI)** — **Avalanche via inverse bremsstrahlung** — **Energy gain** — **Hot plasma**

CCD camera · Plasma · Optical detection · Quartz cell · Telescope · Plasma · Laser beam · Acoustic wave particle counting

The basics of LIBD

Laser-induced breakdown detection (LIBD) is based on plasma formation due to dielectric breakdown in the high-field region of a focused pulsed laser beam when a colloid is present. We commonly experience low-energy plasmas in everyday life, ranging from "flames" over neon lights to the blinding flash of lightning.

The plasma used for LIBD begins with a single (so-called "lucky") electron, which is created by the high-electric field of the laser. In the language of quantum physics, this is equivalent to the nonresonant absorption of four to six photons (multiphoton ionization or MPI) within only some picoseconds. This process is very unlikely, and it takes on the order of 10^{15} photons to free one electron.

By interaction with the electric field, this electron is accelerated (by inverse bremsstrahlung) to energies sufficient to ionize neighboring atoms by means of collisions, resulting in a second electron (second "generation"), which undergoes the same process. Within typically only 30 such generations, a hot, dense plasma is created, which is observed by either its light emission or by detection of the acoustic shock wave generated by its rapid expansion.

Because each plasma event corresponds to one single colloid, the relative number of events per number of laser shots provides a measure of colloid concentration. The photon flux required for breakdown decreases with the increasing number of molecules inside the colloid. By making use of that dependence, the colloid size can be ascertained by varying the laser pulse energy.

A plutonium-242 solution of pure oxidation state (IV) was prepared by electrochemical reduction in 0.5-molar hydrochloric acid to plutonium(III), followed by careful re-oxidation back to plutonium(IV). The oxidation state was monitored by UV spectroscopy and the plutonium concentration was determined by liquid scintillation spectroscopy. The pH was increased with an associated decrease in plutonium concentration by very slow, stepwise dilution with 0.5-molar sodium chloride solution. The pH adjustment ultimately led to the formation of plutonium(IV) colloid kernels, as observed by a well-defined, sharp increase of the LIBD signal. Such colloid formation is the most sensitive indication that the solubility limit has been exceeded.

Macroscopically, the solubility limit is defined as the concentration at which the total amount of a substance is no longer present in ionic form but instead forms a precipitate. Here, our precipitate takes the form of colloids, which are so small that they remain suspended because of Brownian motion.

Analogous experiments were conducted at different concentrations of the plutonium stock solution. With decreasing plutonium(IV) concentration, the pH of colloid kernel formation increased.

Evaluation

Depending on pH, the tetravalent plutonium ion is more or less hydrolyzed, meaning that it is surrounded by up to four hydroxide (OH⁻) molecules. Only in very acidic conditions (a pH less than zero), does a non-hydrolyzed Pu^{4+} aquo-ion exist in solution. The hydrolysis does not change the spectral properties of Pu^{4+}, and so it cannot be detected directly by LPAS. But from the crossing points of colloid formation—log of plutonium(IV) concentration versus pH, we obtain the solubility curve with slope = –2, indicating that the plutonium(IV) dihydroxo complex $Pu(OH)_2^{2+}$ represents the dominant species.

This mononuclear plutonium species undergoes further colloid formation and is thus in equilibrium with colloids. Knowing the hydrolysis constant of $Pu(OH)_2^{2+}$ from the literature, the solubility product (log Ksp = –59 at zero ionic strength) of plutonium colloids (presumably oxyhydrate) can be derived from our data.

Since the amount of plutonium(IV) colloids is relatively small at a given pH of colloid kernel formation, there remains a considerable quantity of (hydrolyzed) plutonium(IV) ionic species undergoing disproportionation with time. This reaction is directly observed by LPAS for plutonium(IV) and (III), at a plutonium concentration within the region of colloid formation above the solubility curve.

The disproportionation reaction can be written as $3Pu(IV) + 2H_2O \rightleftarrows 2Pu(III) + Pu(VI) + 4H^+$, which requires that, for three consumed plutonium(IV) ions, two plutonium(III) ions and one plutonium(VI) ion must be formed. The ratio of plutonium(IV) decrease and plutonium(III)/plutonium(VI) increase should scale as 3:2:1.

Our LPAS measurement however, corresponds to a ratio of 1, indicating a decrease of plutonium(IV) that is too low by at least 50 percent.
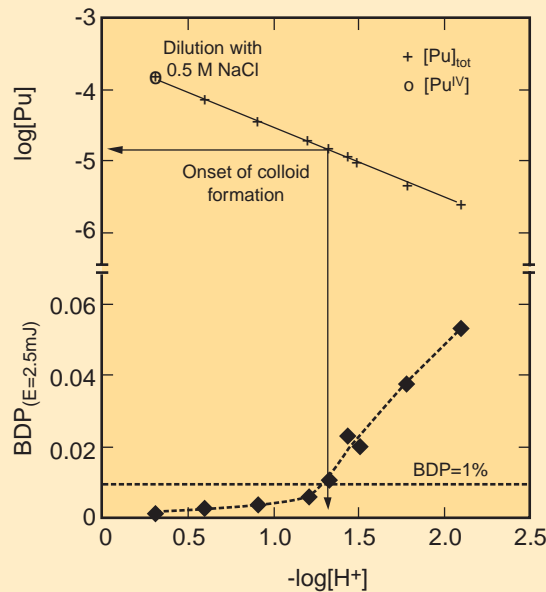
To explain this discrepancy, we must keep in mind that plutonium(IV) colloids are in equilibrium with the plutonium(IV) ionic species, and that the plutonium(IV) tied up in colloids is spectroscopically invisible in the LPAS experiment.
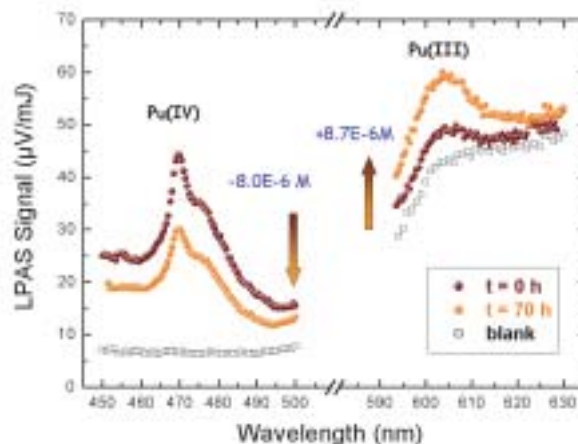
Laser-induced photoacoustic spectroscopy (LPAS) detects the oxidation states of plutonium ions in solution by means of light absorption. This figure shows plutonium(IV) undergoing disproportionation with time. The signal on the left at 470 nanometer (nm) is due to the electronic absorption of plutonium(IV). This signal decreases with time, while the plutonium(III) signal at 605nm increases by the same amount.

Contributed Papers

Diluting a plutonium-242 solution with 0.5-molar sodium chloride results in a decrease in plutonium concentration and an increase in pH (top), until the solubility is exceeded and plutonium(IV) colloid kernels are formed (crossing point). The formation of the colloid kernels is shown by a well-defined, sharp increase of the laser-induced breakdown detection (LIBD) signal (bottom).


The solubility product of plutonium colloids can be derived from the experimental data. For decreasing plutonium concentration, the crossing point of colloid formation is shifted to higher pH. From the slope = −2, we infer the plutonium(IV) to be present as dihydroxo-complex, $Pu(OH)_2^{2+}$, in equilibrium with colloids.
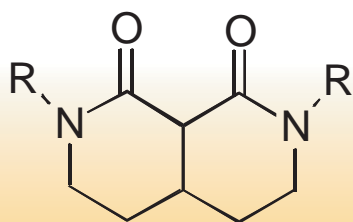

Over the course of 70 hours, as plutonium(IV) ionic species are consumed by the disproportionation reaction, the fraction of (spectroscopically invisible) plutonium(IV) present as colloids redissolved, and this addition to the spectroscopically observable plutonium(IV) fraction was sufficient to account for the discrepancy. Once this was taken into account, the true decrease of plutonium(IV) could be calculated, and satisfied the required 3:2 ratio of the reaction. This was confirmed by LIBD measurements, where the colloid dissolution with time was observed directly.

At lower concentrations (below 10 micromolar total plutonium concentration), LPAS is no longer capable of detecting small amounts of plutonium(IV) colloids present in the solution. However, such minute concentration of colloids (less than one micromolar) can still be detected by LIBD, and the dissolution with time has been demonstrated for solutions of one micromolar total plutonium.

A combination of LIBD and LPAS facilitates a sound assessment of chemical reactions of plutonium(IV) involved at a rim of its solubility-constrained pH for the total plutonium(IV) concentration down to micromoles per liter and for its colloids, about 100 times less (down to a particle concentration of 10 nanomoles per liter).

The present experiment shows how complicated the thermodynamic assessment of plutonium(IV) solubility is. For this reason, there is a wide scattering of the plutonium(IV) solubility product published in the literature—either for its oxide or for its hydroxide, with the differences being a few orders of magnitude. Our research has demonstrated how the use of novel spectroscopic approaches can reduce the uncertainties that have, up to now, hindered the assessment of plutonium(IV) solubility.
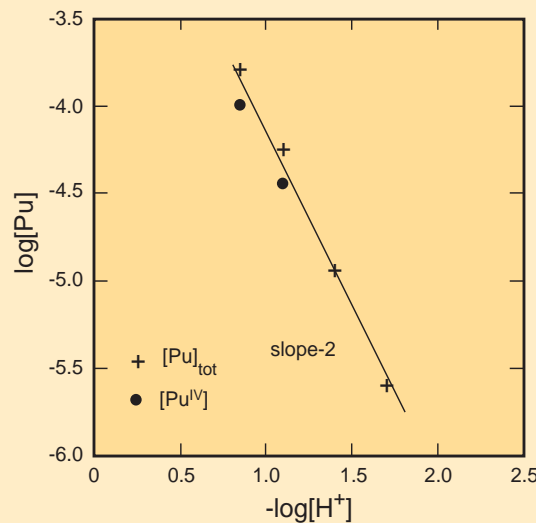
Bicyclic and acyclic diamides

Comparison of aqueous phase binding constants with tetra- and hexavalent actinides

Contributed Papers

Sergei Sinkov

Diamides have been studied extensively as agents for selective extraction of trivalent f-block metal ions from aqueous solutions. They form the basis for separation processes designed to partition the minor actinides from spent nuclear fuel for subsequent transmutation (with concomitant closure of the nuclear fuel cycle) or immobilization (for disposal).

One possible drawback associated with the current generation of diamide extractants concerns the relatively modest actinide distribution coefficients obtained even at high (greater than 1 molar) extractant concentrations. In a recently published report in the *Journal of the American Chemical Society,* we described the extraction characteristics for a new type of diamide molecule. This new diamide (structure **1b**, below) is one million to 10 million times more efficient at extracting trivalent lanthanides and actinides from aqueous solution than previously examined diamides such as tetraalkylmalonamides.

It was assumed that this extraction enhancement reflects superior ligand-metal binding of the bicyclic diamide as compared to acyclic analogs such as tetraalkylmalonamides. A fuller understanding of such structure-function aspects of actinide extraction by amides is needed for the intelligent design of extractants with superior characteristics to those currently available.

One of the possible approaches to quantify the magnitude of ligand-to-metal binding is the application of ultraviolet-visible (UV-Vis) optical absorbance spectroscopy to monitor spectral changes induced by **1a** in the absorption spectra of actinide ions in aqueous solution. The spectral information obtained by varying the ligand-to-metal ratio not only allows estimation of the number of light-absorbing species in solution, but can be used for measurement of the binding (or formation) constants of a ligand with metal ions.

The following sections compare the formation constants for the dimethyl bicyclic diamide (**1a**) and N,N,N',N'-tetramethylmalonamide (TMMA), a related non-cyclic compound, with plutonium(IV), plutonium(VI) and uranium(VI) as measured in the aqueous phase at 1.0-molar ionic strength (HNO_3).

Results with plutonium(IV)

In this experiment, we conducted a spectrophotometric titration by exposing a single portion of a plutonium-239, -240(IV) stock solution (better than 99.5 percent valence purity) to successive introduction and dissolution of either solid crystals (in the case of **1a**) or tiny aliquots of a concentrated stock solution (in the case of TMMA). Neither precipitation nor perturbations in the oxidation state of plutonium(IV) were observed with either ligand throughout the titration procedure at a metal concentration of 8 millimolar (mM).

A new bicyclic diamide ligand architecture optimized for bidentate lanthanide/actinide binding. R = methyl (1a), R = octyl (1b).

*A three-dimensional
structure of the new
bicyclic diamide.
Carbon atoms are
black, nitrogen
atoms are blue,
hydrogen atoms are
light grey, and
oxygen atoms are
red. The vectors on
each oxygen atom,
which indicate the
direction required for
optimal interaction
with a metal ion,
converge in the
computer-designed
structure,
in contrast to
conventional
malonamide with
diverging vectors.*
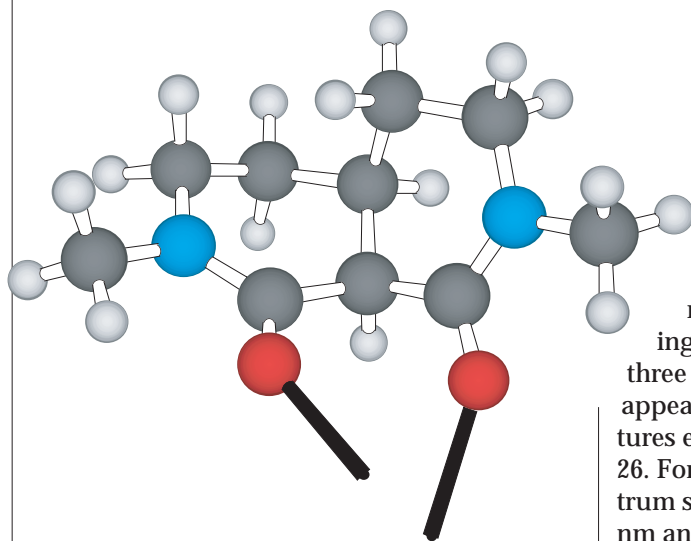
With **1a**, the most significant spectral
changes observed with increasing ligand con-
centration were found in the region of the
main plutonium(IV) peak (a 476→497 nanom-
eter [nm] shift) and in the red part of the
plutonium(IV) spectrum (a 660→684 nm shift
and a 2.4-times intensification of the absorp-
tion band).

Although the spectral changes for TMMA
were similar, we found that such changes were
less pronounced and not identical to those
observed with **1a**. Moreover, these changes oc-
curred at much higher ligand-to-metal ratios.

Using the Singular Value Decomposition
procedure, we found no less than four
complexed species for the plutonium(IV)-**1a**
system and three major complexed species
(and perhaps even a fourth minor species) for
the TMMA-plutonium(IV) system.

Results with plutonium(VI)

Not only was the most intense and sharp
absorption peak of plutonium(VI) at 833.6 nm
monitored for expected complexation effects,
but a wider range (330–950 nm) was examined
to evaluate possible changes in the oxidation
state of the plutonium (initially better than
99.5 percent hexavalent plutonium).

As with plutonium(IV), the **1a** ligand
produced pronounced spectral changes
in the plutonium(VI) spectrum, with
two, new, well-resolved peaks at 840.6
nm and 846.3 nm emerging with even a
moderate excess of ligand. After reach-
ing a ligand-to-metal molar ratio of 80, all
three peaks of plutonium(VI) gradually dis-
appeared. Moreover, several new spectral fea-
tures emerged as shown in the figure on page
26. For example, the visible range of the spec-
trum showed new major peak maxima at 497
nm and 684 nm. This new spectral signature
clearly indicated a reduction of plutonium(VI)
to plutonium(IV) in the presence of **1a**.

A careful redox speciation analysis of the
plutonium(VI) and (IV) spectra showed that
this plutonium(VI) reduction was accompa-
nied by the formation of plutonium(V)—a
weak spectral feature of variable intensity at
568 nm. Once we accounted for the presence
of plutonium(IV) and (V), we used the nonlin-
ear spectra processing routine known as
SQUAD to process the portion of the spectral
set in which plutonium(VI) remains predomi-
nant in terms of concentration. The formation
constants refined from this analysis are shown
in the table on page 19.

In contrast to **1a**, the complexation of
plutonium(VI) with TMMA did not induce
any redox reaction (even after an overnight
contact time). Complexation effects were sig-
nificantly weaker, with the 1:2 complex seen
not as a separate peak but rather as a weak
shoulder in the 842–846 nm range.

Results with uranium(VI)

Both ligands induced significant spectral
changes in the UO_2^{2+} spectrum, accompanied
by a bathochromic shift and intensification of
the absorption bands. Subsequent analysis in-
dicated that **1a** again acted as a much stronger

binding agent than did TMMA. In both cases no spectral evidence was found for formation of higher complexes (1:3 and 1:4 stoichiometry).

Conclusion

Using UV-visible spectroscopy, we have quantified binding constants for both bicyclic and acyclic diamide ligands with plutonium(IV), plutonium(VI), and uranium(VI) in acidic aqueous solution.

This work has yielded three key results. First, we showed that alternating the diamide structure from acyclic to bicyclic increased the overall formation constants with plutonium(IV) by as much as seven orders of magnitude. Second, we found that comparing actinide(VI)-ligand binding affinities reveals enhanced binding to uranium(VI) versus plutonium(VI). And third, the plutonium(VI), but not uranium(VI), in the bicyclic diamide triggers reduction of plutonium(VI) to plutonium(V) and (IV).

We are already at work evaluating the formation constants of TMMA and **1a** with actinides in the +3 and +5 oxidation states.
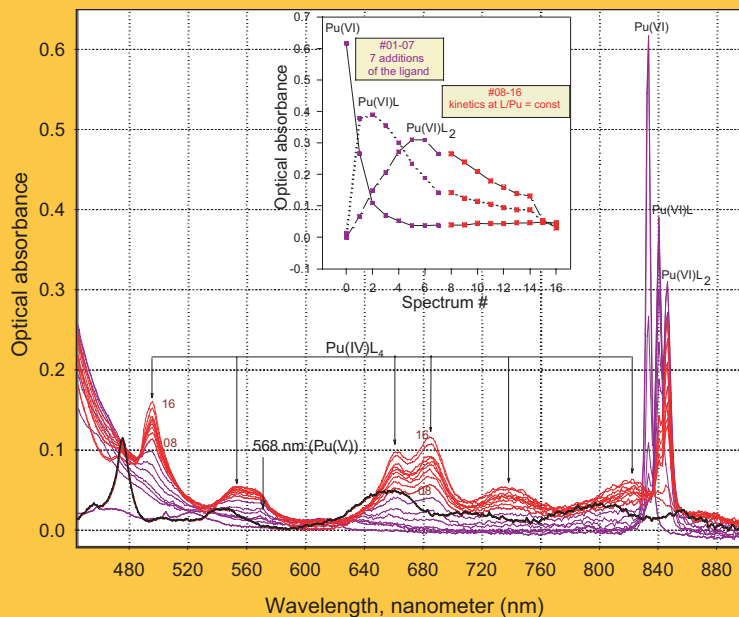
*The spectrophotometric titration of plutonium(VI) by **1a** in 1.0-molar HNO_3. Spectra shown in dark pink correspond to seven successive additions of the ligand up to L/M =80. Red spectra are kinetics of the plutonium(VI)L+plutonium(VI)L$_2$ reduction to plutonium(IV)L$_4$. Black trace shows the reference spectrum of plutonium(IV) with no ligand present at the same acidity and metal concentration as the initial spectrum of plutonium(VI). The kinetic series spectra 08, 09, 10, 11, 12, 13, 14, 15, and 16 were taken at zero minutes, 10 minutes, 20 minutes, 30 minutes, 40 minutes, 52 minutes, 63 minutes, 150 minutes, and 24.5 hours, respectively, after the last addition of the ligand.*

*A summary of all the refined formation constants resulting from this work. Conditional formation constants of plutonium(IV), plutonium(VI), and uranium(VI) complexes with **1a** and tetramethylmalonamide in 1.0-molar HNO_3 at 23±0.5º C. Values in brackets represent one sigma standard deviations.*

Complexant	Species	$\log\beta_{ij}$		
	M_iL_j	Pu(IV)	Pu(VI)	U(VI)
1a	1:1	4.42 (0.08)	2.36 (0.04)	2.85 (0.02)
	1:2	7.95 (0.14)	3.34 (0.07)	4.61 (0.05)
	1:3	10.36 (0.13)	-	-
	1:4	11.48 (0.14)	-	-
TMMA	1:1	2.56 (0.08)	0.44 (0.01)	1.00 (0.01)
	1:2	4.08 (0.11)	-0.03 (0.03)	0.97 (0.03)
	1:3	5.01 (0.14)	-	-
	1:4	4.50 (0.38)	-	-

This article was contributed by Sergei Sinkov, Brian Rapko, and Gregg Lumetta of Pacific Northwest National Laboratory (PNNL); and James Hutchison and Bevin Parks of the Department of Chemistry, University of Oregon, Eugene.

Contributed Papers

Joe Wong

Landmark experiment opens up new research opportunities in actinide science

Researchers use high-resolution inelastic x-ray scattering and a microbeam approach to determine the first full phonon dispersion curves ever measured for any plutonium-bearing materials

This article was contributed by Joe Wong, Daniel Farber, Florent Occelli, Adam J. Schwartz, Mark Wall, and Carl Boro of Lawrence Livermore National Laboratory; Michael Krisch of the European Synchrotron Radiation Facility, Grenoble, France; and Tai-C. Chiang and Ruqing Xu, of the Department of Physics and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign.

Editor's note: The six scientists from Lawrence Livermore National Laboratory (LLNL) who co-authored this article have garnered an award for their groundbreaking research. The team recently received a Science and Technology Award, the highest honor granted by LLNL for science and technology accomplishments.

Understanding the physical basis for the intriguing properties of plutonium materials such as force constants, sound velocities, elasticity, phase stability, and thermodynamic properties critically hinges on the ability to produce high-quality experimental data. Of these, phonon dispersion curves (PDCs) are key to the elucidation of many of these physical phenomena.

A phonon is a lattice vibration, the acoustic equivalent of a photon, the basic quanta of light. PDCs in plutonium and its alloys have defied experimental determinations for the past forty years because of the inability to grow the large single crystals (at least a few cubic millimeters in volume) necessary for inelastic neutron scattering (INS) measurements. Another obstacle was the high thermal-neutron absorption cross section of the most common isotope, plutonium-239.
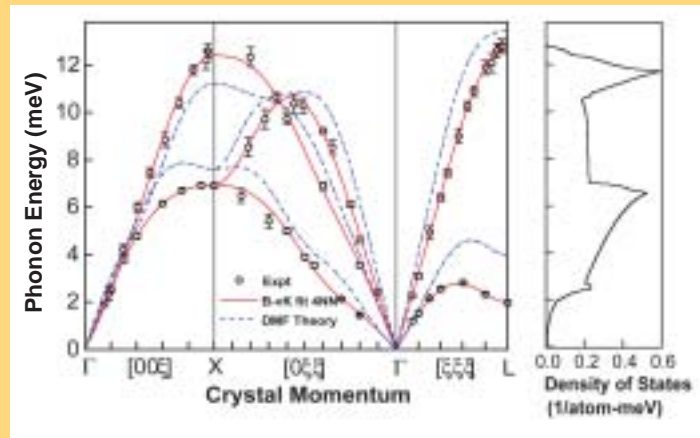
Furthermore, only recently have theoretical computations of plutonium PDCs begun to overcome the difficulties in treating the f electrons accurately within the standard first-principles methods. Thus, the PDCs for plutonium-bearing systems have remained essentially unknown experimentally and theoretically.

The experimental difficulties associated with INS are circumvented in our experimental approach by employing inelastic x-ray scattering (IXS) with milli-electron volt (meV)

energy resolution. With the advent of highly brilliant x-ray sources and high-performance focusing optics, samples with volumes as small as one ten-thousandth of a cubic millimeter can now be studied. These capabilities have opened up new experimental opportunities for materials that are only available in small quantities, as is the case for many actinide systems. The research is covered in detail in a paper published in August in *Science* magazine (see *Science*, Volume 301, page 1078 [2003]).

Our samples were large-grain polycrystalline specimens prepared from a plutonium-gallium alloy containing about 0.6 percent by weight of gallium produced by a strain-enhanced recrystallization technique. To extract the phonon energies, the spectra were fitted by convolving the experimentally determined resolution profile with a model function consisting of a Lorentzian for the elastic contribution and a pair of Lorentzians, constrained by the thermal phonon population factor, for the inelastic part.

The resulting PDCs along the three principal symmetry directions in the face-centered cubic (fcc) lattice are displayed in the figure below,

together with a fit using a standard Born-von Kármán (B-vK) force constant model. An adequate fit to the experimental data is obtained if interactions up to the fourth-nearest neighbors are included and the calculated phonon density of states derived from the B-vK model is also shown. The dashed curves are recent dynamical mean field theory (DMFT) results.

The elastic moduli calculated from slopes of the experimental phonon dispersion curves near the G point are: C_{11} = 35.3 ±1.4 giga pascal (GPa), C_{12} = 25.5 ±1.5 GPa and C_{44} = 30.53 ±1.1 GPa. These values are in excellent agreement with those of the only other measurement on a similar alloy (1 percent atomic weight gallium) using ultrasonic techniques as well as with those recently calculated from a combined DMFT and linear response theory for pure delta-plutonium.

The small difference between C_{11} and C_{44} is very unusual for a metal with a face-centered cubic structure. The shear moduli C_{44} and C' = $(C_{11} - C_{12})/2$ differ by a factor of six. This is in contrast to that of a "normal" fcc metal such as aluminum: 1.2, and is significantly higher than

values in other "unusual" fcc metals such as gamma-cerium: 2.8, lanthanum: 4.1, and thorium: 3.6.

Published results support the conclusion that delta-plutonium–gallium is the most elastically anisotropic fcc metal known. Furthermore, we observe a large deviation, D, from the Cauchy criterion. Our measurement yields D = $(C_{44} - C_{12})/C_{12}$ = 0.9, which differs significantly from zero and implies that the interatomic forces have a strong noncentral component.

The most striking feature of the experimental PDCs is a soft-mode behavior for the TA branch along [111]. A similar feature (but occurring at about twice the energy and at a higher crystal momentum toward the L point) is also seen in a recent DMFT calculation for delta-plutonium. The cubic fcc crystal structure of delta-plutonium can be viewed as being composed of hexagonally close-packed atomic planes stacked along the [111] direction with a specific stacking arrangement. The soft transverse mode at L suggests that each atomic plane could easily slide relative to its immediate neighboring atomic planes to form new stacking arrangements.

Phonon dispersions along high-symmetry directions in a face-centered cubic plutonium-gallium alloy containing about 0.6 percent by weight of gallium. The experimental data are shown as circles. Along the [0ξξ] direction, there are two transverse branches [011]<01-1>(T$_1$) and [011]<100> (T$_2$). Note the softening of the TA[ξξξ] branch toward the L point. The lattice parameter of our samples is a = 0.4621 nanometer. The solid curves are the fourth-nearest neighbor Born-von Kármán model fit. The derived phonon density of states, normalized to three states per atom, is plotted in the right panel. The dashed curves are calculated dispersions for pure delta-plutonium based on dynamical mean field theory (DMFT).

Joe Wong and his colleagues used the high-resolution inelastic x-ray scattering beam line at the European Synchrotron Radiation Facility in Grenoble, France, (shown above) to obtain the first-ever experimentally determined phonon dispersion curves of a plutonium alloy. ESRF is a third-generation synchrotron, and the only facility with a beam line capable of measuring plutonium's lattice vibration energy.

Pure delta-plutonium, on lowering temperature, transforms into the gamma phase, which has a face-centered orthorhombic structure. This structure can be described in terms of a stack of slightly distorted hexagonally packed atomic layers, and indeed is the type of structure that could be easily obtained by layer parallel shear in the fcc phase.

Thus, the soft mode at L is likely a key feature associated with the delta-to-gamma transition, even though this transition is suppressed by gallium stabilization in the present case. This notion is indeed substantiated by the fact that the first interplanar force constant (derived from the B-vK model) of the T[111] mode is more than an order of magnitude smaller than those of the transverse modes in the other two directions.

The small amount of gallium in the sample is sufficient to allow the system to bypass the gamma and beta phases and make a transition directly to a monoclinic alpha-prime phase at about -110°C. The alpha-prime phase, despite its apparent complexity, is also a slightly distorted hexagonal close-packed structure, and is easily accessible from the fcc phase through the same shear mechanism.

A similar soft-mode behavior has been observed in gamma-cerium and lanthanum. In those cases, the transition leads, instead, to a double-hexagonal-close-packed structure, but the same general concept of layer parallel shear applies.

As evident by the data presented in the figure on the previous page, our IXS experiment validates the main qualitative predictions of a recent DMFT calculation for delta-plutonium in terms of a low shear elastic modulus C', a Kohn-like anomaly in the T_1[011] branch, and a large softening of the T[111] modes. Such experimental-theoretical agreements give credence to the DMFT approach for the theoretical treatment of 5f-electron systems. However, while there is good qualitative agreement between theory and experiment, quantitative differences are evident. These differences provide the benchmark for refined theoretical treatments and further experiments with plutonium and other 5f elements.

International team of researchers employs
high pressure to probe bonding in actinide metals

Investigations of protactinium and americium metals provide important insights into actinide bonding concepts

Contributed Papers

Richard Haire

The science question

Pressure, like temperature, is an important variable in the chemistry, physics and materials science of materials. It has been found that the f electrons of the actinide elements—the so-called 5f-electron series of elements—are also greatly affected by pressure. At atmospheric pressure, protactinium, uranium, neptunium, and plutonium have itinerant 5f electrons (electrons involved to varying degrees in the metallic bonding), and they exhibit unusual low-symmetry structures and properties. In contrast, the transplutonium metals normally have localized 5f electrons, display symmetrical structures, and their bonding consists of three non-f-electron conduction electrons (i.e., "trivalent metals"). In this regard they mimic the lanthanide metals.

One obvious difference between these f elements across the series is seen in the variation of their atomic volumes at normal pressure, as shown in the figure at right. The similarity of the trivalent, localized 4f- and 5f-electron metals' volumes contrasts with the behavior exhibited by the four itinerant 5f-electron metals (i.e., protactinium-plutonium). The latter have much smaller atomic volumes in addition to their lower crystal symmetries.

Oak Ridge's Dick Haire discussed research by an international team on the use of high pressure to probe actinide bonding.

The three divalent f-element metals—europium, ytterbium, and einsteinium—are special cases, and result in part due to their higher f-electron promotion energies.
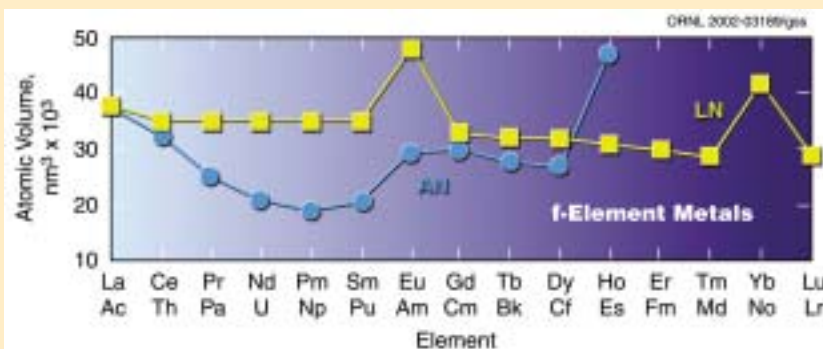
With the some of the early lanthanide metals, it is interesting to note that after acquiring 4f-electron character in their bonding by applying high pressures, they adopt some of the same low-symmetry structures exhibited by the protactinium-plutonium metals that have itinerant 5f electrons. This immediately raises the question of whether applying pressure on the transplutonium metals, which have localized 5f electrons, can bring about significant changes in their bonding.

As these actinides have more spatially extended f electrons than their lanthanide homologs, it should be easier to force their 5f electrons to become bonding by applying pressure—that is, they may be more sensitive to the affects of pressure than their lanthanide counterparts.

Atomic volumes of the f-electron elements reflect differences in bonding present for the elements. The smaller volumes for the protactinium-plutonium metals reflect their itinerant 5f-electrons.

Selecting the f-electrons for study

Studies of the actinides can be difficult, given their varying levels of radioactivity and availability. Of interest to researchers is the potential for forcing increased bonding in the actinides by applying pressure. For example, can pressure force divalent einsteinium metal (element 99) to acquire a third bonding electron? Basically, can pressure force one element to mimic the bonding, properties, and structures of another—a sort of modern alchemy?

Two actinides were selected for recent experimental studies to probe these questions. One study involved americium and a more recent study involved protactinium. (Reports have been published in *Physics Review Letters,* Vol. 85, 2961; Phys. Rev.B, 63, 214101, (2001) and 67, 134101, 2003.) The behavior of these two metals under pressure is of special interest; the studies looked at the actinide elements that "initiate" and "complete" the "dip" seen in the actinide volume curve in the figure on the previous page.

Protactinium has the distinction of being the first actinide metal with a 5f electron (actinium and thorium have d-electrons), and it already has partially itinerant 5f electrons. In contrast, americium is the first element in the series having fully localized 5f electrons at atmospheric pressure, following the four preceding actinides that have itinerant 5f electrons.

These recent studies were conducted to determine if pressure can force additional 5f-electron bonding in protactinium—making it more like uranium—and if pressure can force the onset of 5f-electron bonding in americium—making it behave like the protactinium–plutonium metals, or specifically, its near neighbor plutonium.

An international team of scientists from Oak Ridge National Laboratory, the European Institute of Transuranium Elements, the European Synchrotron Radiation Facility and the Vienna University of Technology carried out the studies.

The researchers examined the structural behaviors of the protactinium and americium up to pressures as high as 130 giga pascals (GPa) using different types of diamond anvil cells to generate static pressures on the metals through different transmitting media (silicon oil or liquid nitrogen). Pressure calibrations employed ruby fluorescence, and/or copper or platinum metals via their known equation of states. Modern diffraction techniques employed multiple wavelengths of high-intensity radiation from the synchrotron and charge-coupled device (CCD) detectors.

What was found experimentally?

The research found that the tetragonal structure of protactinium at atmospheric pressure, where itinerant 5f-electron behavior in the bonding already exists, converts to an orthorhombic structure at about 77 GPa that is isostructural with that of alpha-uranium.

At this pressure, the protactinium's atomic volume is reduced to about 62 percent of that at atmospheric pressure. Accompanying this first-order transformation from the protactinium-I (Pa-I) to protactinium-II (Pa-II) crystal structure is a small relative volume collapse of 0.8 percent. It is postulated that structural transformation with pressure (the Pa-I to Pa-II transformation) reflects an acquisition of additional 5f-electron character in the metallic bonding and alters its basic properties.

With americium under pressure, it was determined that the delocalization of its 5f electrons occurs in two steps, with the progressive formation of lower-symmetry crystal structures (i.e., the third and fourth structures). Overall there are three phases changes up to 100 GPa; the first change from double hexagonal close-packed (dhcp) to face-centered cubic (fcc) represents only a second-order phase change. In the first transition involving delocalization (third phase, Am-III), americium acquires the structure of gamma-plutonium—an orthorhombic structure (space group Fddd)—at about 10 GPa, this structure is accepted as reflecting itinerant 5f-electron character.
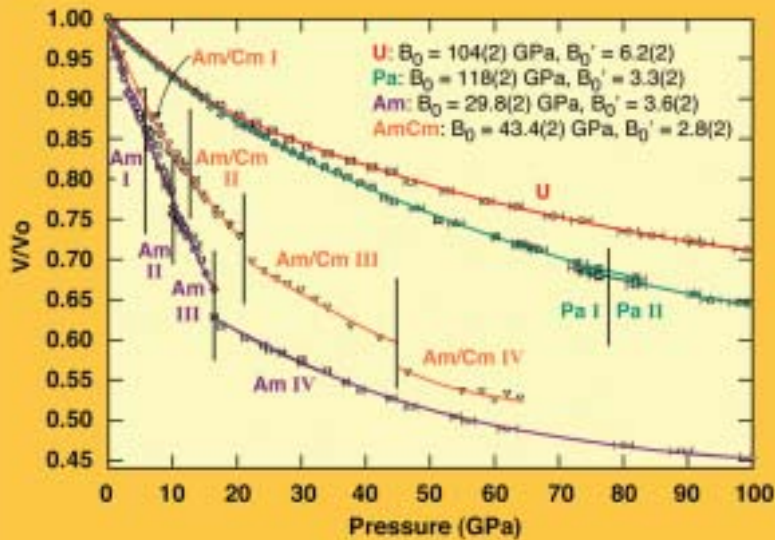
This first-order transformation (Am-II to Am-III) is accompanied by a small but significant relative volume collapse of about 2 percent, which signifies that a change in bonding occurs. It is followed by formation of a fourth phase (Am-IV), a primitive orthorhombic structure (space group Pnma) at about 18 GPa and exists up to 100 GPa. The latter is closely related to a Cmcm structure, the alpha-uranium structure and the Pa-II structure); this structure is also accepted as reflecting the presence of itinerant 5f electrons in the metallic bonding. Accompanying the formation of Am-IV is a more significant relative volume collapse of about 7 percent.

Thus, pressure has forced the delocalization of the 5f electrons in americium after its atomic volume and interatomic distances are reduced considerably (at 100 GPa the volume is about 46 percent of that at atmospheric pressure). Under pressure, the Am-II phase becomes like plutonium (its near neighbor), and at higher pressures, americium then adopts the alpha-uranium structure.

An important difference between the two metals is that americium starts out having fully delocalized 5f electrons, while the 5f electrons of protactinium already exhibit some 5f-electron itinerancy at atmospheric pressure. Both acquire additional 5f character in their bonding with pressure. This initial difference is reflected in specific behavior and properties under pressure. Comparisons between the compression and structural behaviors of americium, uranium, and a 50 atomic percent americium-curium alloy with pressure are shown in the figure on page 26.

The more compressible nature and overall volume reduction of americium metal is due to it starting as a fully localized 5f-electron, trivalent metal, whereas uranium and protactinium initially have itinerant 5f electrons. The figure on page 27 also shows that the slope of the compressibility curves for alpha-uranium, Pa-II, Am -IV, and the 50 atomic percent (Am,Cm)-IV structures (i.e., in the high-pressure regions where they exist) are all very similar, as they should be, given that all have either an alpha-uranium or a closely related structure.

The latest published calculations based on theory for the behavior of americium under pressure were in agreement with this experimental work. In addition, Per Söderlind (LLNL) and Olof Eriksson of the University of Uppsala, Sweden, have also used a calculational approach involving Gibb's free energies to predict a series of structural transformations for protactinium metal under pressure (see *Physics Review B,* Vol. 56, 10719, 1997).

U: B_0 = 104(2) GPa, B_0' = 6.2(2)
Pa: B_0 = 118(2) GPa, B_0' = 3.3(2)
Am: B_0 = 29.8(2) GPa, B_0' = 3.6(2)
AmCm: B_0 = 43.4(2) GPa, B_0' = 2.8(2)

A comparison of the compression behavior of uranium, protactinium, americium, and a 50 atomic percent americium-curium alloy is shown. Bulk modulli and pressure derivatives extracted from the data are also given. (Adapted from the Journal of Condensed Matter Physics, *Vol. 15, S2297, 2003.)*

Our recent experimental work on protactinium confirmed their prediction that an alpha-uranium structure would be formed under pressure from the body-centered tetragonal form, with the differences between experiment and theory being only at which pressure and at what relative atomic volume the Pa-I to Pa-II transition occurs. However, the story for protactinium remains incomplete, as theory predicts that additional structural transformations will occur at much higher pressures (presently difficult to reach experimentally). It will be a difficult but interesting challenge to try to reach these ultra high pressures to confirm the theoretical predictions.

Additional Aspects

Several other pieces of important information can be acquired from such experimental pressure studies (i.e., the bulk modulus and its pressure derivative acquired by applying the Birch-Murnaghan equation of state). In a simple picture, the bulk modulus indicates the "stiffness" of a structure's lattice—the more rigid the structure, the less compressible it is, and the more likely contains a greater degree of bonding. Bulk modulli and pressure derivatives are given in the figure at left for americium, uranium, protactinium, and the americium-curium alloy. Note that the modulus for americium is about 29 GPa (derived from the Am-I phase), while those for alpha-uranium and the Pa-I structure are more than 100 GPa.

It can be informative to compare the compression behaviors of the different metals, the pressures at which structural transformations occur, and the overall picture of the relative volume behaviors.

The close relationship between the body-centered tetragonal structure of protactinium (Pa-I) and the orthorhombic Cmcm structure of alpha-uranium can be seen in the figures at right. The main difference between the structures occurs from a buckling of the "chains" in the latter due to the "y" parameter of the 4c sites of Cmcm. When the Pa-I structure changes to the Pa-II structure, the "y" parameter of the Pa-II structure differs by less than 0.02 from that of alpha-uranium.

The Am-IV structure also shows a close similarity to that of alpha-uranium; it is only necessary to shift the position parameter "z" of the Pnma structure 4c sites to zero from "z=0.10." The three structures in the top of the figure at right show the close relationship that exists between the four phases. The structural sequence for americium metal under pressure is shown in the lower part of that figure. The first two transformation processes basically involve changes in the stacking sequence of planes; and the formation of the Am-IV structure requires an additional "buckling" of the hexagonal planes.

Special facets of americium and protactinium

Important changes in the role of the 5f electrons in the actinides can be extracted from perturbations in their atomic volumes and the structures displayed under pressure. The work on americium and protactinium metals under pressure have shown that pressures increases the itinerant (bonding) nature of their 5f electrons. The onset in (americium) or increase in (protactinium) delocalized 5f-electron character reduces the atomic volumes of the metals, as well as producing structures of lower symmetry. In contrast, heating plutonium reduces the 5f-electron contribution and increases its atomic volume (over that due to expansion).

Using a simple picture, plutonium becomes more like the localized 5f-electron metals upon heating and americium becomes more like plutonium under pressure. Both changes reflect the changing influence of the 5f electrons in the elements' bonding.
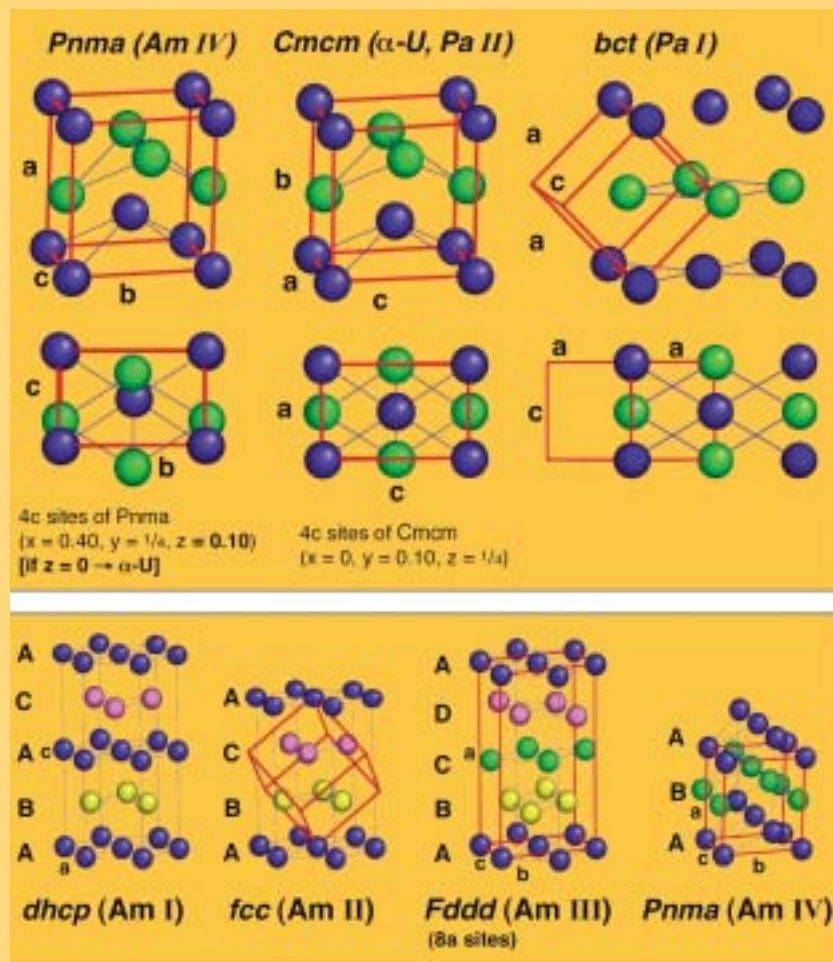
Structures of selected actinides under pressure. The similarity of the protactinium-II and americium-IV structure to that of the alpha-uranium structure is evident. The lower segment shows the structural sequence of americium under pressure to 100 giga pascals.

Future experiments

A number of experiments are envisioned to further explore the actinide metals under pressure to better understand the science that is occurring. Certainly, studies under higher pressures are desired to explore the potential for an onset of new interactions that may drive the formation of new structures and alter the bonding.

There is also the need to study actinide elements with higher Z values using these improved experimental techniques, and both curium and californium metals are two potential candidates. Their behavior under pressure will be affected by the withdrawal of their 5f electrons from their Fermi edges, due to the increased nuclear charge. The latter should make it more difficult to force the delocalization of their 5f electrons, and should require higher pressures to bring about.

Einsteinium is the highest actinide for which such pressure experiments can be envisioned, given the quantities of actinides expected to be available. The behavior of this metal under pressure would be very interesting to study, but it is also an exceptionally difficult material to study because of the very short half-life and intense radiation of its most available isotope (einsteinium-253).

An attempt to study this metal under pressure was unsuccessful, due to crystal destruction by its self-irradiation. A special interest in einsteinium's behavior under pressure is that, in principle, this divalent metal could be forced by pressure to become a trivalent metal like the americium through californium elements at atmospheric pressure. With additional pressure, it may be possible to force einsteinium's 5f electrons to delocalize, perhaps displaying the behavior observed with americium metal under pressure. One can also easily envision numerous other studies of actinide alloys and/or compounds under pressure.

Conclusion

Studies under pressure can provide important insights into the 5f-electron behaviors and their changing roles. It appears that orthorhombic structure-types (i.e., alpha-uranium or the closely related Pnma structure-type) are encountered under pressures in the region of 100 GPa. Whether this type of structure is a dominant high-pressure structure in this region remains to be determined. Theory predicts more symmetrical structures may again be encountered at even higher pressures, due to an increase in dominance of electrostatic interactions and Born-Mayer repulsions.

These studies with americium and protactinium metals will not only help other researchers to better understand the bonding and electronic structure of two elements, but also that of other actinides. They should enable the development of important systematics concerning the actinides. The experimental data should also serve as a platform from which one may evaluate and fine-tune theoretical predictions, thereby enhancing the overall understanding of these complex actinide metals. In addition, such research may contribute to an improved understanding of other elements in the Periodic Table.

Process may have advantages over traditional cleanup methods

Researching the phytoremediation of plutonium

Contributed Papers

Christy Ruggerio

This article was contributed by Christy Ruggiero, Elise Deladurantaye, Brandy Duran, and Stephen Stout of Structural Inorganic Chemistry (C-SIC); and Scott Twary of the Bioscience Division Szilard Resource (B-3).

Phytoremediation—using plants to clean up the environment—relies on the fact that plants are essentially solar-driven pumps, transpiring water from their roots through their leaves. In the process, they can degrade organic chemicals and stabilize contaminants in their root zone, or even take up contaminants into their leaves, thus allowing them to be removed from the soil.

Phytoremediation has distinct advantages over traditional cleanup methods: it is safe, relatively inexpensive, usually simple to implement with existing agricultural practices, and has a positive public image.

Phytoextraction takes the process a step further; it relies on metal-accumulating plants to actually take up metals into their aboveground parts, thereby removing toxic metals from soils and water. Metal-loaded plants are harvested, dried, ashed, composted, or stored. The volume of resulting waste is generally a fraction of waste produced by many current, more invasive remediation technologies, and associated costs are much less.

Most research on metal phytoextraction has focused on finding naturally occurring plants that can take up a large amount of metal compared to their biomass (called hyper-

Elise Deladurantaye, a student in the Structural Inorganic Chemistry Group (C-SIC), checks to see if barley plants have enough nutrient solution to grow for one more day before being harvested to determine their uranium uptake levels. The barley seeds are first sprouted on a small water-soaked mat and then transferred to a nutrient-rich growth solution, where they grew hydroponically in a controlled-atmosphere growth chamber in a Chemistry Division laboratory. The bottles containing the plant solutions are equipped with an air bubbler inlet to make sure the growth solution doesn't stagnate and a HEPA-filtered outlet. The plants grow in the nutrient solution with either no iron, normal iron levels, or high iron levels (well-fertilized). After adjusting to the iron levels for one week, a solution of uranium is added to the nutrient solution and the plants grow in (and take up) the uranium. The plants are harvested by clipping off the stems and the roots and letting them completely dry in small vials. The dry plant parts are digested in acid and then analyzed for uranium content using ICP (Inductively-coupled Plasma atomic emission) spectroscopy and compared to uranium concentration standards.

Phytoremediation of metals has been particularly successful. A few techniques are being explored commercially, including phytostabilization and phytoextraction.

Phytostabilization relies on the plants to decrease contaminant migration by decreasing wind and water erosion of soils, while the plants pull soluble species into their root zone where metals can be sorbed onto roots and stabilized.

accumulators), and then developing these plant species through genetic alteration for improved field performance, and for a wider range of metal uptake.

Work with hyperaccumulators has focused on commercially produced "heavy" metal contaminants—such as lead, mercury, chromium, cadmium, zinc, copper, arsenic, and nickel—rather than radionuclides such as plutonium,

Graminaceous plants produce and release phytosiderophores, a family of nonprotein amino acid that enhances solubility and uptake of iron and possibly other metals from the environment. Phytosiderophores are derivatives of mugineic acid. Shown here is the mugineic acid family of phytosiderophores, nicotianamine (a phytosiderophore biosynthetic precursor), EDTA, and citric acid.

thorium, and uranium. These groups of metals are chemically very different, so it is unlikely that any known hyperaccumulators will be able to hyperaccumulate plutonium or other actinides. Researchers have even speculated

Mugineic Acid   EDTA

Avenic Acid A   Citric Acid

Distichonic Acid   Nicotianamine
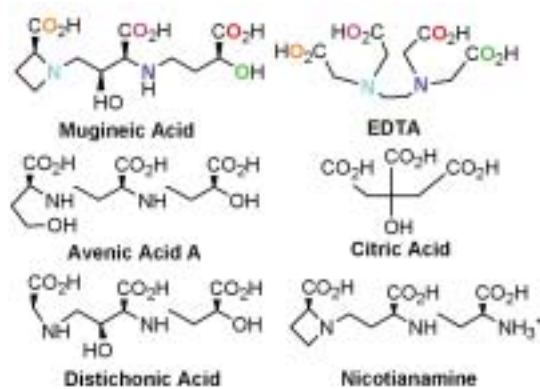
that no hyperaccumulator will ever be found for the actinides.

Fortunately for actinide phytoremediation, true hyperaccumulators are not absolutely necessary. A plant with high biomass but a lower percent of metal uptake will remove the same amount of metal from the soil as a plant that has low biomass (such as most hyperaccumulators) but a higher percent of metal uptake.

Maximum efficiency is still achieved by increasing the percent of metal uptake into the plant. This can be done by increasing the metal solubility, increasing the ability of the metal to cross the root membrane, and increasing the amount of metal translocated into the higher plant parts.

Increasing metal solubility alone has been shown to dramatically improve phytoextraction efficiency. Chelators such as EDTA or citrate are added to soils to improve metal solubility and increase plant uptake, a process called chelate-enhanced, or induced, phytoextraction. For example, researchers at

Phytotech Inc., a metal phytoremediation company, published work in "Environmental Science and Technology," [1998, 32(13), 2004] showing that added citrate can increase plant uptake of uranium more than 1,000-fold.

Unfortunately, adding such chelators can backfire. Even though they increase metal solubility, the rate of metal translocation into the plant roots may still be limited. This can lead to large amounts of solubilized metals that are not able to get into the plant, leading to increased soil migration and leaching to ground waters. Luckily, there may be a better way to "trick" plants into taking up plutonium, or at least trapping it in the plant root zone.

Plutonium behaves similarly to iron, a necessary nutrient in biological systems. Both iron(III) and plutonium(IV) readily hydrolyze, have rich redox chemistry, have high coordination numbers, have similar charge-to-radius ratio, and often have predictably similar binding affinities for the same chelating ligands. Both have extremely low solubility in the environment. Successful development of many plutonium complexation and decontamination agents has relied on this iron-plutonium similarity by exploiting iron chelating ligands.

We hope to be able to use plant iron-uptake systems to trick plants to take up large amounts of plutonium, or at least trap it in the plant root zone.

Graminaceous plants (grasses such as barley, oat, and wheat) produce and release phytosiderophores, a family of nonprotein amino acid that enhances solubility and uptake of iron and possibly other metals from the environment (see figure at left). Phytosiderophores, all derivatives of mugineic acid, form stable complexes with numerous metals.

Phytosiderophores have been shown to enhance soil mobility of copper, iron, manganese, and zinc as much as microbial

siderophores and more than some synthetic chelators. Some researchers have shown that phytosiderophores are up to 100 times more efficient than anthropogenic or bacterial iron chelators for iron uptake into graminaceous plants, presumably because they are the chelate form recognized by the plant roots. They are notably similar to EDTA in structure and metal-binding chemistry. Both have multicarboxylate chelating groups and form extremely strong complexes with iron and other transition metal ions.
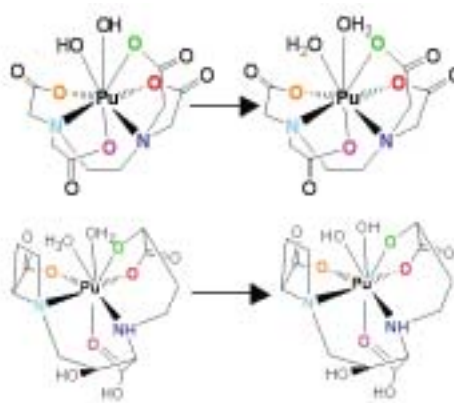
We have examined the binding of plutonium(IV) to mugineic acid over a large pH range using ultraviolet-visible (UV-Vis) spectroscopy (see figure above). Mugineic acid prevents hydrolysis and precipitation of plutonium(IV) to a pH greater than 10; spectra of plutonium(IV)-EDTA and plutonium(IV)-mugineic acid are nearly identical at all but the highest pH. In this pH range, plutonium(IV)-EDTA is believed to be a hydroxo rather than aquo complex, as it is under acidic pH.

The plutonium-mugineic acid complex may not undergo this change, or it may occur at an even higher pH. Possible structures of the plutonium(IV)EDTA and plutonium(IV)-mugineic acid complex are shown in the figure at right. These data suggest that mugineic acid will be as powerful a ligand as EDTA for keeping plutonium species soluble in the environment. We are currently directly testing the rate
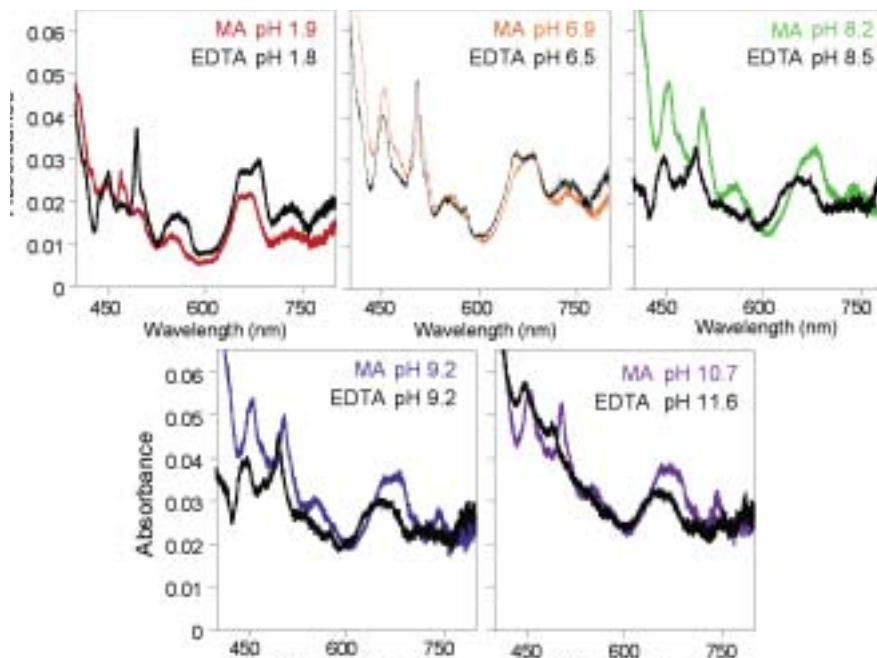
at which phytosiderophores solubilize plutonium hydroxides in comparison to EDTA and the resistance of plutonium-phytosiderophore complexes to microbial degradation.

To investigate whether we can use this iron-uptake system for plutonium and other actinides uptake into these plants, we need to know if plants recognize and take up actinide-

Initial tests with uranium show some interesting results. Barley plants were grown in hydroponic solutions with 1,000 parts per million uranium with or without citrate; without added iron, with 7.5 micromoles added iron ("normal"), and with 100 micromoles of added iron ("high"); and at a pH of 5 and 6. Error bars show one standard deviation among the three to four plants grown at each condition.
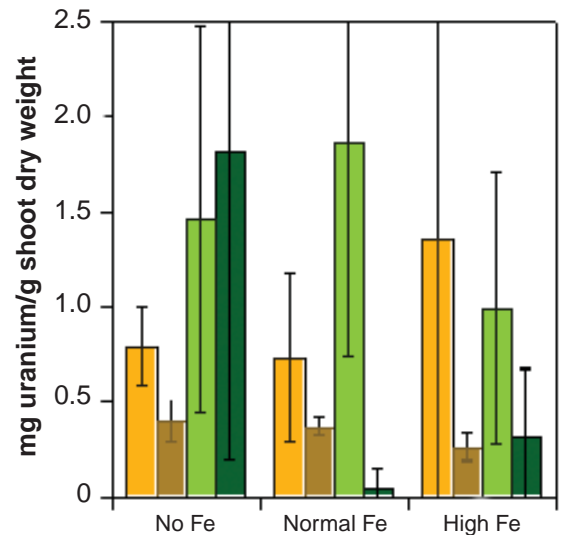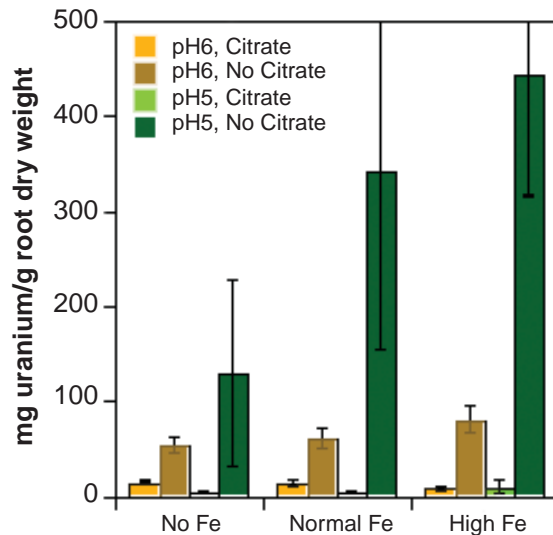
siderophore complexes or whether they are trapped in the plant root zone. Alternatively, we need to know if phytosiderophores create soluble species that aren't taken up or broken down, and therefore contribute to plutonium migration.

To test if phytosiderophores can aid in actinide uptake, we are examining the effects of plant iron status. Iron-starved plants produce more phytosiderophores than iron-saturated ones, and have dramatically higher uptakes of zinc, nickel, manganese, copper, and even cadmium (under some growth conditions), than do high-iron nutritional plants.

We are growing both a phytosiderophore-producing plant (barley) and a non-phyto-siderophore-producing "hyperaccumulator" species (Indian mustard) under variable iron conditions, and with actinides added as various chelated forms (phytosiderophore-chelated, citric acid-chelated, and unchelated) to see how this affects uptake into the plant.

Our initial tests with uranium show some interesting results. Barley plants grown in hydroponic solutions with 1,000 parts per million uranium with or without citrate have low uranium uptake into plant shoots (typically 0.2–3.5 milligrams per gram plant dry weight), with no consistent response to plant iron status, presence of citrate, or pH (pH 5 or 6), although on average, uptake with citrate was slightly higher (see figure above). This was surprising because we expected citrate and decreased pH to cause significantly higher shoot uptake because of their ability to keep uranium soluble. We did not expect the iron status of barley plants to have a major effect on uranium uptake into shoots because, although the phytosiderophore could contribute to uranium solubility, it is unlikely the iron(III)-phytosiderophore uptake system in plants would recognize and take up a uranium(VI) phytosiderophore complex.

Barley plant roots have very high sorption of uranium from solution, as has been observed with other plant species. We observed values from 4 milligrams uranium to more than 600 milligrams uranium per gram dry root weight—one to two orders of magnitude more than in shoots (see figure on page 32). Interestingly, we did observe a significant difference in root uranium binding based on growth conditions.

Barley roots have significantly more uranium bound without citrate present than with citrate, regardless of pH and iron status. This could simply be due to increased precipitation of uranium onto the roots without citrate. However, without citrate present, roots bound significantly more uranium at pH 5 than at pH 6. This may be caused by such rapid precipitation of uranium from solution at pH 6 that it is unavailable for interaction with the plant roots. And at pH 5, roots of plants with excess iron bound more uranium than roots of plants grown without iron. This could have many causes. There could be increased microorganism presence on the "high-iron" roots increasing sorption of metals, or there could be increased solubilization of uranium on the roots by chelators, such as phytosiderophores, when plants are iron starved.

We will soon test plutonium uptake into plants under these same conditions, where we expect iron status and phytosiderophores to make significant differences. We now know phytosiderophores are good chelators for plutonium(IV), and have a good chance of being recognized by the iron-uptake system of the plant because of the similarities between iron and plutonium.

If plutonium-phytosiderophore complexes are recognized and translocated by the phytosiderophore uptake system in plants, plutonium solubilization may be balanced with uptake, eliminating a problem of chelate-induced phytoextraction.

Phytosiderophores may also improve translocation into higher plant parts. Their biosynthetic precursor, nicotinamine, is ubiquitous in plants and is believed to affect cation (copper, iron, zinc, and manganese) mobilization and distribution in plants, presumably having a direct influence on plant metal uptake and translocation.

Even if efficient uptake into the higher parts of the plant cannot be achieved, we will determine how phytosiderophores will affect phytostabilization. Phytosiderophores will chelate actinides. These chelated actinides could be fluxed to the root zone of the plant, as are other metal-phytosiderophore complexes, and could have increased precipitation onto the plant roots. Concentrating contaminants and fixing them onto the plant roots may help prevent migration and improve the efficiency of phytostabilization. Alternately, phytosiderophores could chelate actinides and prevent precipitation onto plant roots, thereby increasing the risk of contaminant migration.

We think this research holds enormous potential. Grasses grow anywhere and everywhere, from arid and semiarid sites, like the Nevada Test Site and the Rocky Flats Environmental Technology Site, to wet and subtropical sites like Oak Ridge National Laboratory and the Savannah River Site.

Plant uptake of plutonium

Plant uptake of actinides is well documented, particularly from past research on human health impacts of nuclear weapons use and testing. We know far more about plutonium uptake into plants from these past studies than we know about other actinides. Relative plant uptake availability for actinides is neptunium > uranium > curium > americium > plutonium, which is a reflection of their solubility under environmental conditions.

Many variables have been shown to affect plutonium uptake into plants: plutonium form and concentration, soil chemistry, soil type, number of successive plantings, plant species, and plant surface area (when fallout and resuspended soil are major accumulation contributors).

As with most metals, it seems that the predominant factor in plutonium uptake from soil by plants depends on chelation of plutonium to increase plutonium solubility. Application of synthetic chelators (EDTA and DPTA), to either soil or hydroponic solutions, has been shown to increase uptake of plutonium up to 1,300 times—resulting in a 20-fold concentration. Ranking of various ligands and counterions for enhancing uptake of plutonium has been shown to be nitrate < acetate < glycolate < oxalate < citrate < EDTA < DPTA, which is a reflection of ligand affinity for plutonium.

Plutonium is translocated from the plant roots into the higher parts of the plants. Plants reduce plutonium(VI) upon uptake. Various studies have shown plutonium is present only as plutonium(IV) (greater than 90 percent) in plant xylem, even if supplied as plutonium(VI). This reduction process may be similar to the purported requirement for reduction of iron(III) to iron(II) prior to root membrane translocation.

These studies also indicate plutonium is transported as an anionic organic complex that is different than the form supplied to root-bathing solutions. In hydroponic studies in soybeans using plutonium(IV) nitrate, xylem exudates analysis of samples with plutonium added both in vivo and in vitro (xylem exudates collected then plutonium added) using anion and cation exchange columns and thin-layer electrophoresis showed that both iron and plutonium are present primarily as organic acid complexes (instead of amino acid or peptide).

Nickel(II) and cadmium(II) were present primarily with components of the amino acid/peptide fraction, again showing the differing uptake and transport systems for hard and soft metals. The forms of plutonium transported in the xylem appear to change with plant age, and the amounts of plutonium parallel essential ion concentrations.

The evidence suggests that plutonium may track the normal plant ligands used for metal uptake and growth. Indeed, it has been suggested that after absorption in the plant, trace contaminants are translocated, metabolized, and stored generally analogously to nutrient elements. In support of this, nutrient elements, especially iron, zinc, and copper, that compete for reaction sites and organic ligands affect the chemical form of plutonium in the plant.

Phytosiderophore-mediated uptake could explain some of the observations made on plutonium uptake into grasses.
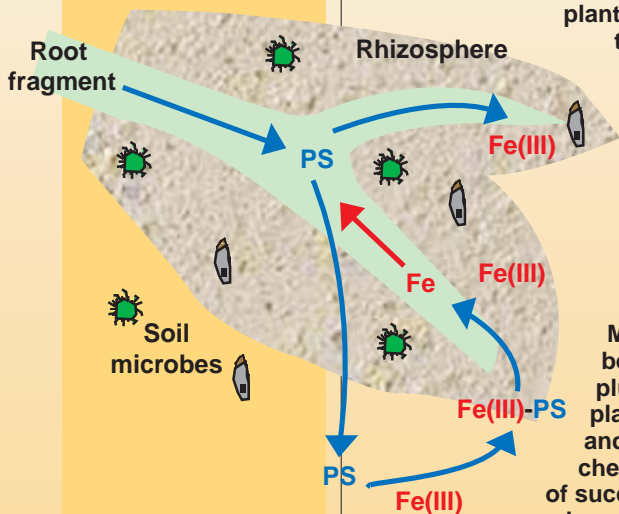
Grasses produce phytosiderophores (PS) to acquire the iron (Fe) they need. Could these phytosiderophores also be used to trick plants into taking up plutonium?

The plutonium phytoremediation process is illustrated.
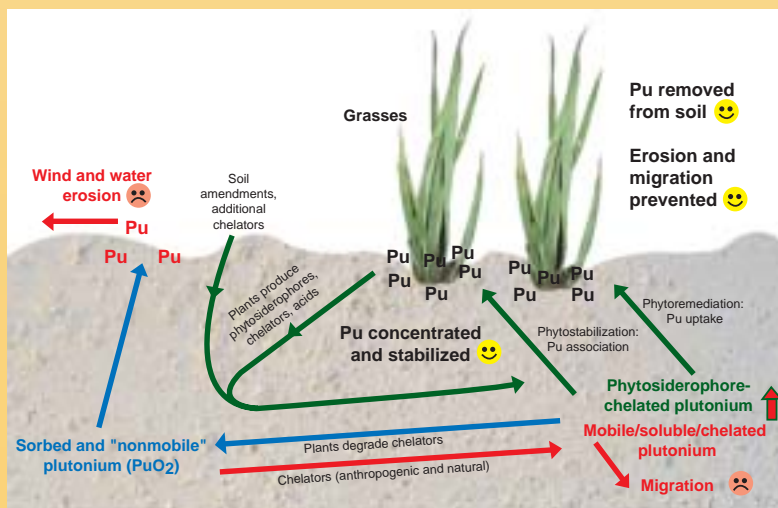
The future of plutonium science
Plenary speakers discuss the many avenues of research

Condensed Matter Physics

A parallel institution to Los Alamos in the sense of its broad diversity of nuclear-materials research, the European Union's Institute of Transuranium Elements (ITU) was ably represented by Gerry Lander at the conference's first plenary presentation.

Lander was enthusiastic in elaborating some novel ITU approaches to the actinide electronic structure conundrum. He described a body of work that employed high pressure to alter the atomic volume in actinides. Displaying compressibility curves for uranium, americium, and an americium-curium alloy, Lander presented evidence for a transition from localized to bonding behavior in americium's 5f electrons when the element was compressed to 50 percent of its atomic volume.

He subsequently described a clever way of performing the reverse experiment, applying negative pressure to a thin deposited film of plutonium to illustrate what he described as a "pseudo phase change" in delta-phase plutonium. While he admitted that the exact interpretation was still controversial, he also enthused, "these experiments are very beautiful, and they give us a nice handle on the electronic structure of plutonium."

Continuing on this theme of understanding electronic structure, Lander described the discovery of superconductivity in plutonium compounds as "the most exciting thing in actinide science for the last fifty years." He was animated about the ITU–Los Alamos partnership, describing it as a collaboration in which the two organizations contributed complementary skills and were continuing to work very closely together.

Gerry Lander

Actinide Compounds and Complexes

Los Alamos staff member Wolfgang Runde of the Isotope and Nuclear Chemistry Group (C-INC) offered a primer in the selected chemistry of actinide compounds, particularly those relevant to modern methods of plutonium purification related to pit manufacturing.

Despite what he characterized as "intensive study of transuranic minerals," Runde emphasized that single-crystal structures of plutonium compounds—particularly those of plutonium(V) and (VI)—remain rare. Because of their importance in plutonium processing and purifications, and in long-term nuclear waste management, his presentation focused on the oxalates, hydroxides, and silicates of plutonium, which despite their importance, are poorly characterized on a structural level.

Wolfgang Runde

*Vic Reis and
Theresa Fryberger*

His talk covered aspects of both the preparation of such compounds and the insights acquired into their molecular structure.

In addition to the wealth of specific information presented in this talk, it also conveyed an overall sense of the interesting and complicated chemistry that keeps actinide researchers engaged in trying to comprehend the myriad of bonding behaviors that actinides display in both laboratory and natural environments.

The Nuclear Fuel Cycle

On Dec. 8, 1953, President Dwight Eisenhower delivered his "Atoms for Peace" speech before the United Nations. Eisenhower's goal was to apply "the miraculous inventiveness of man" to change "the fearful atomic dilemma" into something that could benefit humanity.

Fifty years later, Vic Reis postulated that perhaps it was time to initiate what he called an "Atoms for Peace II." Before he outlined the possible vision for such an endeavor, he noted that this new vision would also be for fifty years, which is equivalent to the lifetime of one nuclear power plant. Reis, of Science Applications International Corp., is a former DOE assistant secretary for defense programs.

Reis' vision emphasized nuclear power. With the construction of a system of next-generation nuclear power plants, electricity could become safe, plentiful, affordable, and environmentally friendly. This extensive growth of nuclear power would require countries to work together to settle regional conflicts and curtail international terrorism and rogue states. Wars would have to be minimized if not eliminated.

Key tasks for the United States include extending licenses of existing nuclear power plants and opening the Yucca Mountain repository, Reis said. The United States government also must help industry with costs associated with construction of new plants, continue the development of the advanced fuel cycle initiative, and design a fourth-generation nuclear reactor. (See ARQ 1st/2nd quarter 2003.)

Materials Science and Plutonium Properties

One of the more interesting characteristics of plutonium is how it ages. In essence, plutonium ages from "inside out" and "outside in," which means that it not only changes its own properties, but also has the potential to change the properties of surrounding materials.

"The three most important aging effects in plutonium are the radiogenic decay of the various plutonium isotopes, the possible thermodynamic instability of the plutonium alloy itself, and the corrosion of plutonium's surface during both storage and function," said Joe Martz of Los Alamos' Materials Science and Technology (MST) Division. "These aging effects accumulate slowly over decades.

Joe Martz

Furthermore, such effects may not take place in a linear fashion."

To ensure the performance, safety, and reliability of the U.S. nuclear weapons stockpile, researchers must be able to predict when aging effects negatively influence a weapon's performance. To accomplish this goal, scientists must understand the properties of plutonium throughout its "lifetime," from the time it is manufactured to the time that it is "retired from service."

"Virtually all conditions in plutonium are ripe to age-related damage," Martz concluded. "Yet, we have found no first-order effects after several decades. Hence, we feel reasonably comfortable that the lifetimes of components will last at least several tens of years."

Actinides in the Environment

Teresa Fryberger, director of the DOE's Division of Environment Remediation Sciences, Office of Biological and Environmental Research, Office of Science, told her audience: "It is clear that we won't be able to remove all contamination at all sites. We must understand what contaminants are mobile and under what conditions."

Such understanding, she said, will make it possible to develop science-based risk evaluations to produce better decision-making; more-effective remediation and containment strategies; and a solid understanding of what, when, and where to monitor at sites in long-term stewardship.

Current actinide research in the DOE weapons complex includes study of uranium migration under the tank farms at Hanford Site in Washington; plutonium transport at Rocky Flats Closure Project in Colorado; plutonium sources and mobility at Savannah River Site in South Carolina; and microbial effects on actinide speciation and mobility.

"We have learned a great deal about the molecular interaction of actinides in the subsurface," Fryberger said. "We have been able to provide scientific data that has impacted remediation decisions for specific problems at specific DOE sites; (but) we have far to go before we can describe the complex interactions and processes that are important in transport."

In the future, she said, scientists must use the available DOE computing capabilities and insert mechanistic and chemical information into models; use interdisciplinary teams to do comprehensive, long-term field studies that include modeling in design and interpretation; and develop improved characterization tools.

Detection and Analysis

Christopher Puxley of the Atomic Weapons Establishment at Aldermaston in the United Kingdom brought scientists up to date on the application of vibrational spectroscopy to actinide analysis.

Vibrational spectroscopy can be used for *in situ* nondestructive analysis of both bulk and trace actinide compounds—notably for the detection and analysis of typical species and unexpected contaminants that occur on the surface of actinides.

Puxley made three points about using fiber-optic analysis on actinides. First, fiber-optic midinfrared analysis is applicable to organic materials and their degradation products. Its applicability to inorganic compounds is limited to oxyanion identification, low-molecular-weight atoms in materials (e.g., hydrides), and low-molecular-weight, multiply-bonded anions.

Second, fiber-optic Raman analysis is applicable to both inorganic and organic materials. It is extremely useful for the identification of inorganic compounds but is difficult to apply to compounds that are black.

And third, because of its high sensitivity and small spot size, fiber-optic Raman spectroscopy is a valuable technique to detect contamination and surface species on bulk materials.

—Vin LoPresti,
Octavio Ramos, Jr.,
and Charmian Schaller

Christopher Puxley

Helen Caldicott and Sig Hecker
Point/Counterpoint

Point

Helen Caldicott, founder of Physicians for Social Responsibility, sketched out a very dark picture of plutonium and nuclear weapons in a speech that opened the "Actinides in the Environment and Life Sciences" portion of the conference.

She told her audience of plutonium scientists—many of them from the nuclear weapons laboratories—that, "Plutonium is incredibly carcinogenic." Sufficient exposure, she said, kills cells, and the cells that survive are "likely to have mutations." The resulting genomic progression of instability can continue for more than 30 generations.

Caldicott, an Australian pediatrician with a specialty in cystic fibrosis, said, "We find out what radiation does by doing decent epidemiological studies," but not enough epidemiological studies are being done at autopsy, partly because of their expense.

Helen Caldicott

She mentioned new work being done by Alexander Miller at the Armed Forces Radiobiology Research Institute in Bethesda, Maryland, John Little at the Harvard School of Public Health, and Eric Wright at the University of Dundee in Scotland on "the bystander effect"—the development of genetic mutations by cells on the periphery of tissue exposed to radiation.

She said that plutonium in the particulate form that is less than five microns in diameter can be inhaled. It can settle into the lower part of the lungs, where it can cause mutations. About five tons of plutonium was released into the atmosphere during weapons testing, she said, and one result is that, "We are increasing genetic disease by the contamination of the atmosphere with plutonium," and contamination lives on in the genes.

Plutonium, which has a 24,000-year half-life, was first made for nuclear weapons. Caldicott said she knew some of the early scientists who worked on the bomb, but, "I became terribly alarmed about what they did."

And she concluded, "I'm talking to you as a physician, as a pediatrician … You must stop building nuclear weapons! … I don't know if you've got 10 more years."

Counterpoint

Helen Caldicott's views on nuclear weapons did not go unchallenged. Sig Hecker, Los Alamos Senior Fellow, rose from the audience to present "another point of view."

Hecker, a plutonium metallurgist, said, "You brought us back to reality because the last few days, we were having great fun…. I appreciate your point of view. I happen not to agree with it." And, he said, the viewpoint of plutonium scientists is "not less noble in terms of service to humanity" than Caldicott's.

He said that if one looks at the statistics, about a million people died as a result of wars in the 1500s and 1600s. In the first half of the 20th century, 87 million people died in wars. "Soon," Hecker said, "we would have found a way to wipe ourselves off the face of the Earth." However, in the last half of the 20th century there was a dramatic drop in the number of deaths. "In science, we call that a discontinuity . . . a discontinuity in the death of mankind," said Hecker. This was an apparent reference to Caldicott's lack of scientific data in her discussion.

Sig Hecker

"Nuclear weapons got mankind to think differently," Hecker said. "I view it as a good thing that occurred during the buildup of nuclear weapons." The question now, he said, is, "How does one manage significantly reducing the number of nuclear weapons without the number of deaths sneaking up once again?"

Death due to war
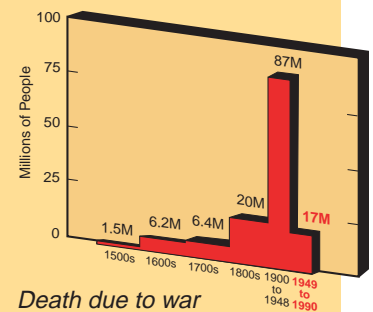
Caldicott said, "I know you say you developed nuclear power to maintain the peace, and it was a good idea, but you don't know" whether those weapons will eventually be used. She said she believes that unless mankind abolishes nuclear weapons, "there will be a nuclear war" somewhere, someday because of the "fallibility of human minds."

Jon Schwantes of Lawrence Berkeley National Laboratory asked Caldicott whether she had developed any figures on the transport of plutonium particles and their resulting danger as compared to the transport and resulting danger of smoke particles.

She said the risk of plutonium to workers is "quite high," and, "The amount of plutonium in the world is huge." She asked, "How can you quantify something that lasts half a million years?" Schwantes said, "You can do risk assessment." The exchange continued, and Schwantes concluded, "If there's no chance of the plutonium coming to your lungs, then there's no risk…."

—*Charmian Schaller*

Panel discussion
Five views on opportunities and constraints for actinide research

Monday evening's panel discussion brought together five preeminent names in actinide science: Graham Andrew, of the International Atomic Energy Agency (IAEA); Theresa Fryberger, head of the DOE's Division of Environment Remediation Science; Gerry Lander of the Institute of Transuranium Elements (ITU) in Karlsrühe, Germany; Senior Los Alamos Fellow and former director Sig Hecker; and Vic Reis of Science Applications International Corp. (SAIC). The discussion was moderated by Los Alamos' Ed Arthur.

Gerry Lander: There are tremendously exciting prospects for actinide science . . . but there are also some fundamental problems that we, as the actinide people, should address. The first is: how do we as institutes that have special capabilities share those capabilities with people on the outside?

The pressure's on us from the institutional aspect to reduce the number of places, to reduce the flexibility at those places. And at the same time, we have to reach out to other people, because otherwise, this field is going to get smaller and smaller in the funding eye. Somebody, today, made the comment that age profile at this conference is much better . . . much younger. Bringing in students and showing them things can be done is another crucial aspect that we have to be fully aware of.

The other thing that has personally frustrated me is an institutional problem again. Transport of our materials has become an absolute nightmare. In the old days we used to carry around bits of uranium. I never went anywhere without bits of uranium in my suitcase. Now that's absolutely forbidden.

And, you know, there are people who think . . . that a milligram of uranium will kill a whole province in France. You can't somehow get across to these people that there's uranium all over the place.

But the transport now, especially post-September 2001, has become more difficult. There's been a total crackdown. And that just means collaboration between the labs is cut again. So there's this huge tendency to reduce things, to cut us off from the outside.

Let me just say a bit about reactor future. And all the countries, in my view, are not collaborating enough. I think there is good commercial reason for that. There is, of course, a lot of money in nuclear fuel . . . and so there is a lack of collaboration, which is driven partly by money. But in the end, if there is not collaboration, we all go down together. I would like to see a more-open forum on discussing the pros and cons of those fuels rather than this sort of internal battling that seems to be going on all the time.

I am enormously distressed by the huge cuts that we are seeing in our neighboring institutions, and the whole atmosphere that we see in many European countries with a working nuclear power system—a constant reduction. It's not just because of the waste legacy, but also because of the whole question of how the third world fits in . . . for power and for raising the standards of living.

Gerry Lander

Panel Discussion

Vic Reis

Vic Reis: The future of civilization really depends upon how actinides, and specifically plutonium, are managed over the next fifty years. It's that important; I don't think there's anything *more* important. I come at this from both the perspective of national security and global climate change. And if you think about the major things that can occur over the next fifty years, how one deals with actinides, plutonium in particular, will be key to much of that.

I worked twenty years ago in the Office of Science and Technology Policy in the White House. I was really impressed with the astronomy community, because what astronomy did then—and I suspect, still does—is that they argue a lot among themselves. But they then present a unified research agenda, and that makes life a lot easier for the people in the Office of Management and Budget and those people in the National Science Foundation who have to put the policy together for Congress.

What I've learned over the past four years since I've left the warm confines of the nuclear weapons complex and moved out in to the broader world is that it's very hard to get a unified research agenda.

I suspect that we have a good many of the entire community right here at this meeting. The good news, right, is that there aren't very many of you. The bad news is that you can't seem to figure out what to do. At least by the time it reaches the Department of Energy and Congress, it's so complicated that the interplay between the politics and the research community frequently gets destroyed. But the research community ought to be able to figure... out what that agenda is; and if they do that,

much of the politics will . . . I won't say take care of itself . . . but it will be a lot easier.

Theresa Fryberger: If you look at the cleanup efforts of the weapons complex in the United States, a lot of people would say that this has not been as successful as it might have been. And part of the reason is because they don't know where contaminants will go; they don't know how they behave; they cannot predict risk.

If we're hoping to make a place for clean nuclear energy or safe deposition of waste, we need to understand this. We've studied the transport of contaminants for several decades, particularly for Yucca Mountain. And people ask: "Well, why don't we know more?" One reason is that, until about a decade ago, we didn't have the ability to do things like speciation and actual environmental samples that we're now able to focus on. So we really

Theresa Fryberger

couldn't understand at the molecular level what the real chemistry was. We've made great progress over the last decade, but we need to continue to make more.

So where do I think we need to go in environmental sciences in the near future? Scaling is an issue; we need to get beyond the molecular level. We need to make more progress, both temporal and spatial. We need better characterization techniques in the field . . . and we need to focus science a little bit differently. We need long-term comprehensive field studies that are conducted by teams—dedicated teams of scientists from various disciplines. And we need to use modeling, both for designing experiments as well as to model systems.

Sig Hecker: The near future? It's the f electrons that are exciting and that's one of the exciting challenges—just exactly what are the f electrons doing? And that's going to be heard a number of times: that plutonium sits right at that knife edge between the very different kind of behavior—bonding or localized . . . you know, participating in the process or being chemically inert. And we still have lots of years of exciting research to try to soak that up.

To me, actinides mean new materials, new behavior, and new thinking. Personally, what's been of greatest interest . . . what's so interesting and fascinating is plutonium's instability. We saw today the enormous gyrations that they find as a function of temperature with all the six allotropes. So it's unstable with temperature but it's also very unstable with pressure. Then with the six allotropes—when you start squeezing on them—those high volume states start to squeeze out, and then, with any actinide, you may end up with interesting results in the crystal structure. But if you get the right chemical additions like gallium and aluminum, you can stabilize nice metallic crystal structures.

Unfortunately, the problems of proliferation and terrorism threaten to set back all our efforts for decades. There's a great need for international collaboration. Meanwhile, there's the Patriot Act . . . supposed to be keeping terrorists out, and is keeping academicians out instead.

Russia is a huge environmental laboratory, and we should be over there taking advantage of things they've done wrong. It illustrates that it's almost impossible, today, to get experimental work done.

Graham Andrew: What I've been hearing from my colleagues . . . and I agree . . . is that the basic science is driven by both strategic and policy requirements. We must make a decision early on and go from basic science to the next step. Yet we can't pursue all options.

An example of crucial decision-making is the area of waste. Unless we resolve repository and waste-management problems, we won't be proliferating weapons, but rather, Yucca Mountains.

Beyond plutonium, we need to improve our capabilities in minor actinide science. Minor actinide science needs to be taken forward in the next ten years; we need new forensics. Do we have the same understanding of, for example, solution chemistry for the minor actinides as we do for plutonium?

We need much better international cooperation with respect to fuel-cycle options. For example, do we want to proliferate reprocessing plants or coalesce those efforts into, for example, having three or four such facilities around the world?

Most important, we need to be concerned about capturing the knowledge base that already exists . . . dealing with capturing the knowledge of people leaving the field. Else, we risk squandering what is an irreplaceable resource.

Sig Hecker and Vic Reis

Synthesis of New Plutonium Main-Group Metal Materials

Peter K. Dorhout,[1] Ryan F. Hess,[2] Kent D. Abney,[2] and Steven D. Conradson[2]

[1]Colorado State University and [2]Los Alamos National Laboratory
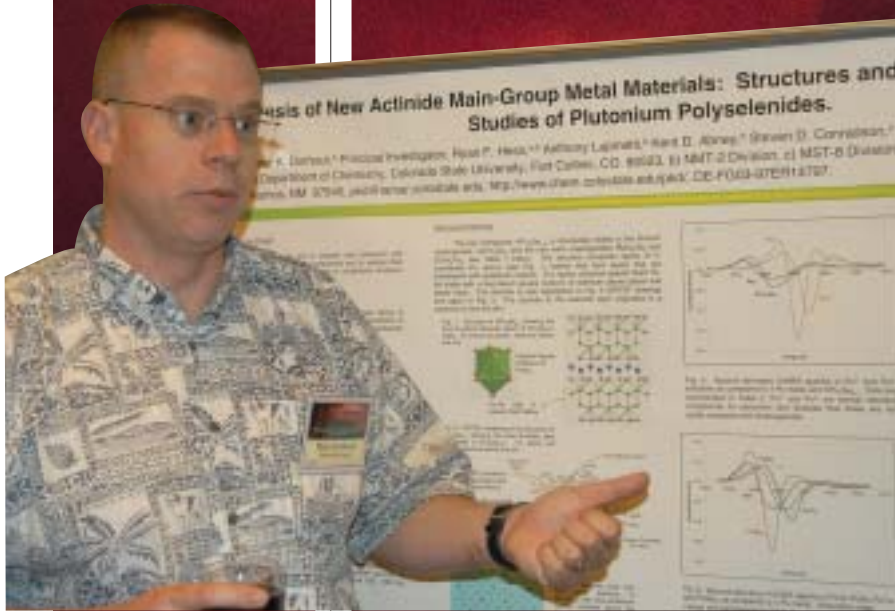
**Peter
Dorhout**

"This project focuses on understanding the electron density around plutonium in a variety of different matrices," explained Peter Dorhout, a professor at Colorado State University. "We prepared a new compound this past year that has plutonium in a selenium matrix. The selenium chan share electron density in a 'balancing' fashion. That is, depending upon what the plutonium metal 'wants,' the selenium can either accept electron density or push electronic density onto the metal."

This new compound has the formula KPu_3Se_{8-x}. To determine the electron density of this new compound, researchers used x-ray absorption near-edge structure (XANES), which provides oxidation-state information about the absorbing, or target, atom. The key result from this work was that the absorption edges of such heavy chalcogenide systems appear close to the value found for plutonium metal (1–2 electron volts). This result implies that the electronic environment around plutonium in this compound is very similar to that found in the metal.

"You really have to understand the electron density around plutonium with the particular ligands before you can make any bold assertions about what kinds of oxidation states you're going to find," said Dorhout. "Most studies have been done in oxides and aqueous solutions, but the real environment isn't always just oxygen or water. So, I think that by digging real deeply into oxidation chemistry, we found some more applicable aspects to our work with respect to how we can better interpret XANES spectroscopy."

—Octavio Ramos, Jr.

The Localized and Itinerant Nature of 5f Electrons in Pu and Pu Compounds

J. J. Joyce, J. M. Wills, T. Durakiewicz, M. T. Butterfield, E. Guziewicz,
J. L. Sarrao, L. A. Morales, D. P. Moore, and A. J. Arko

Los Alamos National Laboratory

Scientists are using photoelectron spectroscopy and a computational mixed-level model to determine the electronic structure of plutonium metal and several plutonium compounds, including materials that have magnetic and superconducting transitions. "We are trying to understand the electronic structure of plutonium in a broader context," said John Joyce of Los Alamos. "To do this, we are looking at plutonium from many different crystal structures and with many different ligands."

By examining a large number of alloys and compounds, these workers have observed the development of a common electronic structure based on the dual nature of plutonium 5f electrons: localized or itinerant.

"From a programmatic standpoint, we're interested in developing an atomic-scale model that shows how oxides and hydrides work with plutonium. Such work is relevant to life sciences and long-term storage issues."

By applying both experimental (photoelectron spectroscopy) and computational (mixed-level model) techniques to describe the electronic structure of a broad range of plutonium materials, researchers at Los Alamos anticipate a much better understanding of the electronic properties of plutonium.

—Octavio Ramos, Jr.
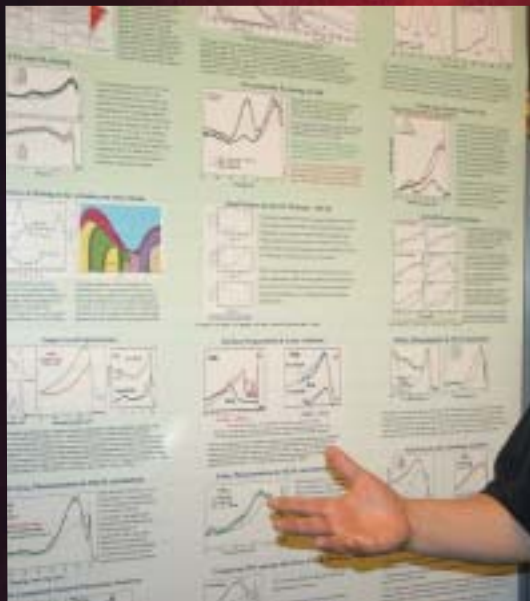
John
Joyce

Plutonium Futures conference

Gerd Rosenblatt

The conference in a nutshell

The "Plutonium Futures—The Science Conference 2003" closed with a tour-de-force summary of the entire five day program by Gerd Rosenblatt, one of the founders of the conference. Rosenblatt, of Lawrence Berkeley National Laboratory, said he listened to all forty-five talks and looked at all 125 posters. "The scientific quality of the papers (presentations and posters) has just gone up and up and up," Rosenblatt said. On the other hand, he commented, the average age of those attending the conference has gone down notably—perhaps as much as 10 years—a fact that gives Rosenblatt "a lot of hope" for the future of plutonium science." Such diverse participation is vital for the field, he said. "This has been an exciting meeting, and we're making exciting progress," Rosenblatt concluded, but he reminded his audience of the call by Dr. Helen Caldicott, founder of Physicians for Social Responsibility, for an end to all nuclear weapons. "We have to think about what we do and why and our responsibilities to our fellow human beings," he said.

Gerd Rosenblatt provided two postscripts for his audience: The next plutonium conference will be the "Actinides 2005 International Conference," July 3-8, 2005, in Manchester, England. To keep up with developments, those interested in the conference should visit the Web site (www.actinides2005.com). And the International Union of Pure and Applied Chemistry and the International Union of Pure and Applied Physics ruled in August that GSI in Darmstadt, Germany, (a heavy ion research center funded by the Federal Government of Germany and the state of Hesse) has proved the existence of another element— number 110. The element, which was discovered in 1994, will be known as "darmstadtium" and have the chemical symbol Ds. Rosenblatt said that GSI has also discovered element 111. But, he said, no other suggested elements yet seem sufficiently reliable to be approved.

Copies of conference transactions available

If you were unable to attend the recent "Plutonium Futures—The Science Conference 2003" but would like a copy of the conference transactions, please contact Meredith Coonley. Send requests via e-mail to <u>suki@lanl.gov</u> or phone 505-667-0392. Please include your name and complete postal address in the message.